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**THE MATERIALS PROCESSING RESEARCH BASE
of the
MATERIALS PROCESSING CENTER**

(NASA-CR-164367) THE MATERIALS PROCESSING
RESEARCH BASE OF THE MATERIALS PROCESSING
CENTER Annual Report (Massachusetts Inst.
of Tech.) 199 p HC A09/MF A01 CSCL 11G

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submitted by

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submitted to

**NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
400 MARYLAND AVENUE S.W.
WASHINGTON , D.C. 20546**

ANNUAL REPORT FOR FY 1980

PREPARED UNDER GRANT NO. NSG 7645



Massachusetts Institute of Technology
Materials Processing Center
Cambridge, Massachusetts 02139
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May 20, 1981

Dr. John R. Carruthers, Director
Materials Processing in Space Division
NASA Headquarters
Room 227, Mail Code EM-7
600 Independence Avenue
Washington, D.C. 20546

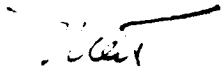
Dear John,

Enclosed is the Fiscal Year 1980 Annual Report of the Materials Processing Center to the National Aeronautics and Space Administration for Grant No. NSG-7645 which is entitled "The Materials Processing Research Base of the Materials Processing Center". Three (3) copies have been sent to Mr. Joe Vitale, the NASA Technical Officer, and two (2) copies have also been sent to the NASA Scientific and Technical Information Facility.

The Annual Report is presented in four (4) sections beginning with a description of the Materials Processing Center and summary of structure, goals, and current activities. Section II presents a general summary of the major thrust areas of the Center -- nucleation and rapid rate solidification, fluid flow in crystallization processes, and adaptive materials processing. Section III reports on the specific research activities within each thrust area which are supported by NASA Grant No. NSG-7645. Section IV outlines the overall materials processing activities at Massachusetts Institute of Technology, many of which benefit either directly or indirectly from the NASA supported activities.

The Materials Processing Center has enjoyed much success during its first full year of operation, having grown from the initial NASA grant of \$300,000 to a current total research volume approaching \$3 million per year. Much of this success is due to both the direct and indirect support of NASA, for which we are most appreciative. We look forward to a continued collaboration with NASA in the materials processing area, a field of critical importance to national productivity and security.

Sincerely yours,


Merton C. Flemings
Director, Materials Processing Center

fmp
cc/Dr. L. Testardi
Mr. J. Vitale

Professor Merton C. Flemings, Director
Room 8-407

Materials Processing Center

School of Engineering

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Cambridge, Massachusetts 02139

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I. INTRODUCTION AND SUMMARY

THE MATERIALS PROCESSING CENTER

The Materials Processing Center was formed within the School of Engineering at Massachusetts Institute of Technology in August, 1979. Center activities encompass all engineering materials including metals, ceramics, polymers, electronic materials, composites, superconductors, and thin films.

The formation of the Center emphasizes the growing interest and involvement of the materials community at M.I.T. in technological problems relating to improved ways of producing and shaping materials so that they can perform more effectively for society's use... and with acceptable economic and social costs.

An important underlying theme of the Center is that performance of materials can be controlled through control of internal structure, from the macroscopic to the atomic level. Another important theme is that economic and low energy production of materials in a competitive world depends on rapid assimilation of many technologies into materials processing, and on modification and adaptation of materials processes to better utilize these technologies. Such new technologies include distributed intelligence, robots, and concepts of systems engineering. The materials processing industries in the United States, long the world leaders, now have segments which are lagging behind those of other countries. Innovative materials processing developments, incorporating advanced technology, are essential if the country is to regain leadership in this area.

The Materials Processing Center has been established at M.I.T. to provide a way for the staff and the faculty

of the School of Engineering, and others, to contribute effectively to broad materials processing problems and opportunities. The Center will interact with industry and government in seeking to develop, extend, and apply the scientific and technological base of materials processing, and to broaden its educational base.

The Center is currently undertaking a broad range of research activities, and is developing new curricula, seminars, and continuing education programs. It encourages and sponsors specialized research and academic appointments, including the extended residence at M.I.T. of industry and government personnel as visiting faculty, adjunct faculty, postdoctoral researchers, etc. Faculty and staff participate in the Center from a number of departments at M.I.T., principally the Departments of Materials Science and Engineering, Mechanical Engineering, Electrical Engineering, and Chemical Engineering.

WHAT IS MATERIALS PROCESSING?

The arena of Materials Processing is the transition or "action" stages of the well-known "Materials Cycle" (see Figure 1). These comprise extraction, processing into bulk materials, processing into engineering materials, fabrication, recycling, and disposal.

Materials Processing is the engineering field that seeks to control structure, shape, and properties of materials, and to do so in a cost effective way with acceptable social costs. It lies at the heart of the broader field of Materials Science and Engineering, linking basic science to societal need and experience (see Figure 2).

For thousands of years, long before Materials Science was dreamt of, Materials Processing was an essential part of

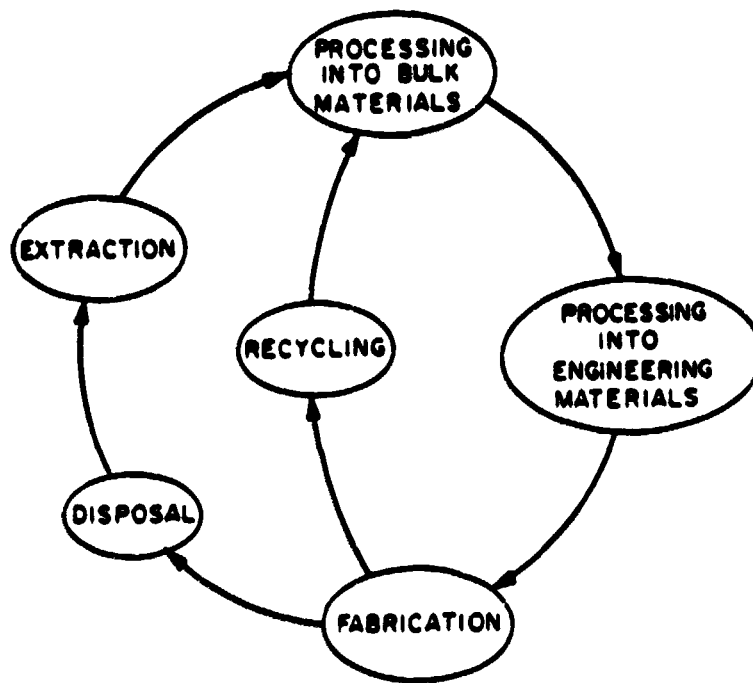


Figure 1. Materials Processing steps, as transition stages in the Materials Cycle. (Taken from the "Materials Cycle" of the Cosmat Report, Materials and Man's Needs)

society, practiced at its best by skilled artisans who worked with materials to advance their utility and aesthetic appeal. For illustrations, we can turn to such well known examples as the pottery, textiles, and cast arts of Asia Minor 5000 years ago, the beautiful and functional Japanese swords, medieval iron-making, and the ubiquitous American blacksmith.

The knowledge of these artisans was empirical, and their processing can be described as "materials craftsmanship". They achieved properties and performance through processing but without basic science and understanding as in modern processing, Figure 2, and without the essential modern concept that properties and performance are controlled through control of structure. Today the crucial role of structure control at all levels (submicroscopic, microscopic, and

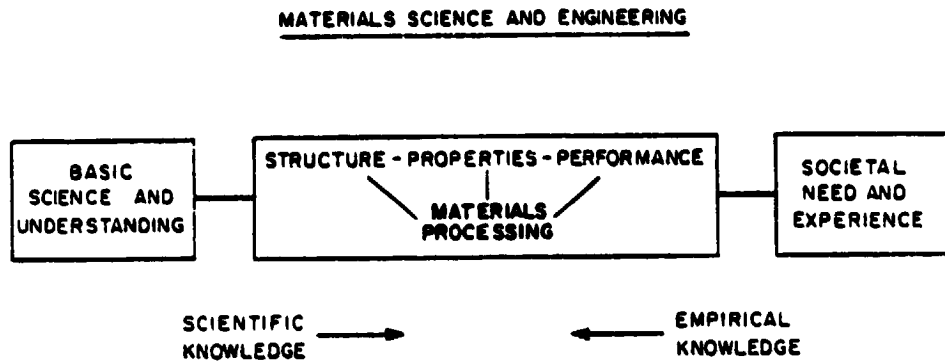


Figure 2. Materials Processing as part of Materials Science and Engineering

macroscopic) is understood, as are the essential linkages of materials processing to the scientific base and to societal needs. Largely as a result of this understanding, materials processing has developed to become a field critical to current national needs. Materials Processing is central, for example, to development and economic production of sophisticated new materials for the energy, transportation, electronic, and aerospace technologies. It is central to improving productivity in materials processing and manufacturing efforts, and to enhancing energy conservation, recycling, environmental protection, and worker health and safety.

THE MATERIALS PROCESSING CENTER AT MIT

If universities are to contribute constructively to the large scale problems of the inherently interdisciplinary field of Materials Processing, they must create groupings of faculty that cut across traditional lines, and groupings that can constructively interact with non-university (i.e., industry and government) personnel. For this purpose, the

Massachusetts Institute of Technology has formed the Materials Processing Center to provide a focus for research and education on the processing of materials, i.e., on processes to produce bulk materials and on those involving change of the shape or structure of materials for better meeting man's needs. The Center addresses process fundamentals, innovation, and design, and concerns itself with related economic and societal issues. It encompasses the following central areas:

- o Process Fundamentals and Applications: Development and application of process fundamentals to improved industrial materials processing operations. Process innovation and control, including nondestructive evaluation. Productivity improvement. Interaction with industry.
- o Materials Systems Engineering: Establishing and optimizing industrial materials processing operations. Dealing with complex issues involved in producing, managing, and conserving the country's materials resources.
- o Societal Issues: Assessment of effects of materials processing operations on society. Process improvement or substitution to minimize environmental impact, energy consumption, health hazards.

The Center is establishing interactions with industry and government in both research and education and is addressing itself specifically to the identification and solution of materials processing problems.

GOALS OF THE CENTER

The major goals of the Center are to:

- o Contribute usefully to the complex issues involved in establishing and optimizing industrial materials processing operations, and in producing, managing and

conserving the country's national resources, by:

- (1) innovating new materials processing techniques;
 - (2) disseminating modern technology and fundamental knowledge;
 - (3) seeking rational solutions to societal and systems problems relating to processing of materials.
- o Improve the relevant scientific base for materials processing by:
- (1) providing research programs for graduate education;
 - (2) developing post-doctorates and junior faculty in processing as an area of professional concentration;
 - (3) expanding the involvement of M.I.T. staff and students in materials processing as an area of professional concentration;
 - (4) educating and motivating professionals for the field of materials processing through development of curricula and educational materials in close liaison with industry personnel.
- o Strengthen institutional relationships among M.I.T., industry, and government.

CURRENT CENTER ACTIVITIES

The Materials Processing Center is organized to enable it to conduct, or facilitate conduction of, three specific types of research programs: (1) discipline oriented research problems of the type ordinarily conducted by an individual faculty or staff member, and his associates and students, (2) technologically related problems that are so broad in scope that they require effective focused cooperation of a team of faculty or staff members, and (3) development of processing "science", or a "materials processing base" that cuts across traditional disciplinary and materials boundaries.

The current annual operating budget for the Center is 2.7 million dollars, of which approximately \$600,000 comprises the central "nucleus" of a broad based grant from the National

Aeronautics and Space Administration. Table I lists the programs of the Center. These cover a wide range of activities that fall within four central thrust areas of the Center -- areas which the Center views as being at the heart of its research charter. These are:

- o Process innovation and development of new materials through processing.
- o Mathematical and experimental modeling of processes.
- o Computer aided processing.
- o Economic issues relating to materials processing.

The research programs of the Center, listed in Table I involve 16 faculty member, 36 graduate students, and 27 staff members. Industrial interaction is a keystone of the Center and a number of programs within the Center involve such interaction. Approximately \$700,000 of the Center's funding is provided by industry.

INDUSTRIAL ADVISORY BOARD AND THE CENTER INAUGURATION

An Industrial Advisory, comprising industrial leaders in materials related industries has been established to guide and advise the Center. The members of this Board and their affiliates are listed in Table II.

The first meeting of the Board was held on the morning of the Inauguration of the Center, February 1, 1980. The Board discussed the Center and its goals, appointed Dr. Maurice E. Shank, Chairman, and during the course of 1980 submitted its thoughts and recommendations in writing to the Dean of Engineering of M.I.T. It is intended for the Board to meet approximately once yearly.

TABLE I
Materials Processing Center
Massachusetts Institute of Technology
Research Projects

Title	Funding Agency	Principal Investigator
Refining by Solidification	ARO	Flemings
Continuous Production of Strip by Rheocasting	DOE	Flemings
Fundamentals of Rapid Directional Solidification	NSF	Flemings
Surface Quality of Steel Ingots and Slabs	AISI	Flemings
Materials Processing Research Base for Materials Processing Center	NASA	Flemings
CO ₂ Laser Crystal Growth Facility	NASA	Haggerty
Rapid Cooling Effects in Polymers	NASA	McGarry
Polymer Melt Processing Operations	NASA	Roylance
High Quench Rate Process	NASA	Grant
Studies of Metals Electroprocessing	NASA	Sadoway
Computer Aided and Adaptive Materials Processing	NASA	Lund
Fluid Flow in Crystal Growth	NASA	Brown
Control of Segregation and Defect Formation during Large Diameter Crystal Pulling of Si	NASA	Witt
Computer Modeling of the Impacts of Technology and Policy Alternatives on the U.S. Stainless Steel Industry	USBM	Clark
Electroslag Castings	NSF	Flemings

TABLE I (continued)

Title	Funding Agency	Principal Investigator
Mathematical and Physical Modeling of the Electrosag Remelting Process	NSF	Szekely
Development of Manganese Base Alloys as a Substitute for Chromium Bearing Alloys	USBM	Clark
Hitachi Grant to Ceramics Processing Laboratory for Fellowship	Hitachi	Bowen
Tektronix Grant to Ceramics Processing Laboratory for Fellowship	Tektronix	Bowen
Heat Source - Materials Interactions during Fusion Welding	ONR	Eagar
A Basic Study of the Role of Convection in Grain Refining with Applications to the Space Processing of Beryllium	NASA	Flemings Szekely
Heat Flow Control and Segregation in Directional Solidification	NASA	Witt
Physics and Chemistry of Ceramic Powder Processing	DOE	Bowen
Colloid Chemistry and Ceramics Processing	Corning	Bowen
Process Ceramic Capacitors	5 Company Consortium	Bowen
Laser Heated C.V.D. Process	Solar Energy	Bowen
Synthesis and Processing of Ceramic Powders	Standard Oil	Bowen
Post Doctoral Fellowship in Ceramics Processing	Union Carbide	Bowen
Strengthening by Fractional Melting	AMMRC	Flemings
	<u>TOTAL FUNDING</u>	<u>\$ 2,216,477</u>

TABLE II

Advisory Board for
Materials Processing Center, M.I.T.

Dr. Turner Alfrey, Jr.
Research Scientist
Dow Chemical Central Research

Dr. Donald J. Blickwede
Vice President and Director
of Research
Bethlehem Steel Corporation

Dr. Kenneth J. Brondyke
Director, Alcoa Laboratories
Aluminum Company of America

Dr. Harris M. Burte
Chief of Metal and Ceramics Div.
Wright Patterson Air Force Base

Dr. John R. Carruthers
Director, Materials Processing
in Space
NASA Headquarters

Dr. Paul A. Fleury
Director, Materials Research Lab.
Bell Laboratories

Dr. Rodney Hanneman
Manager, Materials Characteriza-
tion Lab.
Corporate Research & Development
General Electric Company

Mr. Frank B. Herlihy
Vice President, Group Executive-
Hydraulics
Abex Corporation

Mr. Winston R. Hindle, Jr.
Vice President, Corporate Operations
Digital Equipment Corporation

Dr. John R. Hutchins, III
Vice President and Director
of Research & Development
Corning Glass Works

Dr. Horace N. Lander
Senior Vice President, Research
and Development
AMAX, Inc.

Dr. Robert Mehrabian
Chief, Metallurgy Div.
National Bureau of Standards

Mr. John H. Morison
Chairman of the Board
Hitchiner Manufacturing Co., Inc.

Dr. Richard K. Pitler
Vice President-Technical
Director, Metals Group
Allegheny Ludlum Steel Corp.

Mr. Richard F. Polich
Chairman
Tallix Incorporated

Dr. George S. Reichenbach
Vice President and General
Manager, Materials Div.
Norton Company

Mr. F. James Rechin
Vice President, Turbine
Components Division
Equipment Group
TRW Incorporated

Dr. Edward I. Salkovitz
Director, Materials Sciences
Div.
Office of Naval Research

Dr. Maurice E. Shank
Director, Engineering Tech.
Commercial Products Div.
Pratt & Whitney Aircraft Group
United Technologies Corporation

TABLE II (cont'd)

Mr. Charles H. Smith, Jr.
Chairman of the Board
SIFCO Industries, Incorporated

Dr. M. A. Steinberg
Deputy Chief Scientist
Lockheed Aircraft Corporation

Mr. Thomas R. Wiltse
General Manager, Central Foundry
General Motors

ADJUNCT MEMBERS

Dr. George Mayer
Director, Metallurgy & Materials
Science Div.
Army Research Office

Dr. Edward S. Wright
Director
AMMRC

The afternoon of the day the Advisory Board met was devoted to a colloquium on "Materials Processing -- An Ancient Art -- A New Technology". The program and speakers are listed in Table III. Following a discussion, short addresses were given by Dr. Paul Gray, then President-Elect, M.I.T. and by Dr. Robert Frosch, Administrator, NASA.

Sections II and III of this report describe in some detail the ongoing NASA sponsored "core" research. In addition, for the benefit of the M.I.T. Community and other readers of this report, staff members of the Materials Processing Center have assembled summaries of other Materials Processing Research underway in various Departments, Centers and Laboratories of the Institute. These are included in Section IV of this report.

CENTER RESEARCH HIGHLIGHTS, MPC

Major thrust areas of the broad based NASA sponsored Center grant are (1) convection in solidification processing, (2) nucleation and rapid rate solidification, and (3) advanced computer aided and adaptive materials processing. Professors Robert A. Brown, August F. Witt, Donald R. Sadoway, Warren M. Rohsenow, David K. Royle, and H. Kent Bowen are working, or initiating work, on various aspects of convection in solidification processing. Work is proceeding on metals, semi-conductors, polymers and ceramics. As one example, Professor Sadoway has initiated, as part of the Center, a new Electroprocessing Laboratory. This is an area of research that has been neglected at MIT but is of growing importance with the need for development of energy efficient and environmentally acceptable materials and processes. A second example is work of Professor Witt who is designing and building a new type vertical crystal growth system, with an interactive program on heat transfer analysis with Professor Rohsenow.

TABLE III

**COLLOQUIUM
FOR INAUGURATION OF THE MATERIALS PROCESSING CENTER**

**SCHOOL OF ENGINEERING
MASSACHUSETTS INSTITUTE OF TECHNOLOGY**

February 1, 1980

MATERIALS PROCESSING

An Ancient Art - A New Technology

Chairman Merton C. Flemings
Ford Professor of Engineering
Director of Materials Processing Center

1:30 P.M. MATERIALS PROCESSING IN HISTORY
Cyril S. Smith
Professor of Metallurgy, Emeritus
Professor of the History of
Technology & Science, Emeritus
Massachusetts Institute of Technology

**2:05 P.M. METAL PROCESSING IN A MODERN METAL PRODUCING
INDUSTRY**

Dr. Allen S. Russell
Vice President of Science
and Technology
Alcoa

2:40 PM POLYMER PROCESSING
Dr. Turner Alfrey, Jr.
Research Scientist
Dow Chemical Central Research

3:20 P.M. COFFEE

3:35 P.M. PROCESSING OF OPTICAL WAVEGUIDES

Dr. John R. Hutchins, III
Vice President and Director of
Research & Development
Corning Glass Works

**4:05 P.M. TECHNOLOGY, INNOVATION, AND PRODUCTIVITY.
WHAT IS THE OUTLOOK?**

Dr. Arthur M. Bueche
Senior Vice President
Corporate Technology
General Electric

Professors Nicholas J. Grant, Frederick J. McGarry, Julian Szekely, and Merton C. Flemings are working in the area of nucleation and rapid rate solidification. This is an aspect of materials technology that shows great promise for development of new materials with unique properties, including high temperature materials, ultra-high strength materials, and "glassy" metals. In addition to this NASA sponsored work there is extensive additional work on rapid solidification being conducted by members of the Center. Nine faculty members and a large number of staff and students are working on a total of 26 different projects as described beginning on page 145. An important industrial program on rapid solidification is that recently initiated through the Center by Professors Latanision and Vander Sande, sponsored by Bethlehem Steel Corp.

The Ceramic Processing Research Laboratory, under leadership of Professor Bowen is an important and integral part of the Materials Processing Center. This laboratory was established to develop a processing science base for the ceramics industry. Because of unique institutional problems (at universities, national laboratories and corporations), there has not been a strong base in ceramics processing science as there has been in physical ceramics. Thus, part of the effort at M.I.T. is to form a strong and interactive coalition between M.I.T., the government agencies and the ceramics producer and user industries. Thirteen companies have joined the consortium, over 50 companies have made visits to the campus during the past 15 months to discuss research results, and several companies are making preparations to send their staff members for "internships" in the laboratory.

The laboratories has established the specialized facilities and equipment required for processing particulate ceramic materials. The facilities in the Ceramics Processing

Research Laboratory permit powder materials to be made, modified, characterized, and fabricated into finished pieces. Special glove box and controlled atmosphere pressing equipment have been established for processing high purity non-oxide powders synthesized by a novel laser heated gas phase process. In addition, Center funds have been used to aid in purchase of facilities for melt processing research, i.e. Laser Processing facilities that will also have applicability to materials other than ceramics. Research activities in this area are described beginning on page 110.

Polymer processing comprises a vigorous and growing activity within the Center. Polymer processing, like ceramics processing, has long been regarded as a series of unrelated empirical disciplines dealing with formation and shaping. However, the industry has now come to realize that much is to be gained by taking a consistent view in development of a basic science of polymer processing. Polymer processing activities currently being conducted by faculty associated with the Center are described beginning on page 120.

The Center has been active in supporting and broadening of the materials systems activities of Professor Joel P. Clark. Professor Clark's research combines elements of microeconomics, financial analysis, operations research, and statistical estimation with engineering analysis of the production and utilization of materials. One example of his research activities is a project on "Computer Modeling of the World Stainless Steel Industry". In this work, an engineering based supply model of the production of stainless steel product shapes is combined with an econometric model of stainless steel demand to simulate supply, demand, and price interactions in the international stainless steel market.

In related activities, the Center has been active through Professor Szekely and others in mathematical and experimental modeling of processes. The broad area of application of computer modeling to materials systems and processing is one we expect to continue to grow and develop.

A series of workshops have been held by the Center during this past year to examine computer and robotic applications in materials processing, and to focus on how processes themselves can be altered by these new technologies. The aim of these workshops, led by Dr. Robert T. Lund, is to provide the focus for future work in "Adaptive Materials Processing". In addition Professor Thomas Eagar working with Dr. G. B. Kenney have been exploring the development of joint activities between Center members and others at MIT working in robotics and related areas. We hope during the coming year to initiate activities in this important area. Sections II and III of this report present information on the NASA sponsored "Materials Processing Research Base" which comprises approximately one quarter of the Center research. Section IV then describes the broad range of materials processing research being conducted by faculty associated with the Materials Processing Center.

II. MATERIALS PROCESSING RESEARCH BASE - GENERAL SUMMARY

Research activities conducted under the Materials Processing Research Base during this first year are in three areas: (1) nucleation and rapid solidification, (2) fluid flow in crystallization processes, and (3) adaptive materials processing. These activities are summarized below and are followed by more detailed research abstracts.

NUCLEATION AND RAPID SOLIDIFICATION

Professor Grant's work (with S. Kang and W. Wang) on rapid solidification of high integrity aluminum alloys is concentrating on complex aluminum-lithium alloys. These alloys (rapidly solidified and subsequently consolidated) have the potential for exceptionally high specific modulus as well as specific strength. Current work is on structure-processing-property relations of alloys of the 2020 family with lithium additions in the 1½-3½ range. One of these alloys developed ultimate strength values in excess of 90,000 psi with useful ductility.

Professor McGarry (with Dr. J. Mandell, A. Agrawal and H. Lee) has initiated an innovative program on rapid solidification of polymers and to our knowledge this is the only work in progress to study structure-processing-property relations of polymers cooled at rates greater than about 10^4 °C/sec. During the current year, work is proceeding on development of equipment, refinement of specimen preparation techniques, theoretical calculations, and preliminary experimentation. Experiments to date have been on rapidly solidified polystyrene films. Specimens produced are now being studied.

A third program, with emphasis on nucleation, was initiated at the middle of the current grant year on convection in grain refining, with potential application to space processing. This work is under the joint supervision of Professors Flemings and

Szekely. To carry out portions of the experimental work planned, Dr. Abbaschian has upgraded and modified a levitation melter, and a modified "Perepezko type" apparatus has also been constructed to produce fine droplets of molten metal suspended in molten salts or other liquids. Experiments have been conducted in the levitation melter using nickel-base alloys. Correlations are being developed between undercooling and grain size (and dendrite structure). In addition, theoretical work is underway to calculate electromagnetic forces and fluid flow in levitation melted droplets of given cylindrical geometry coils. A portion of this work is being conducted at General Electric Space Division, sub-contracted as part of this program. This third program straddles the rapid solidification thrust area and the one outlined in the next section on fluid flow.

To enhance capabilities of the Center in processing in general and in rapid solidification in particular, we have invested during the past year, a portion of the equipment funds from this grant in a Laser Processing Facility. These funds, combined with those from other sources, have enabled purchase and installation of a \$200,000 facility. This facility will give to M.I.T. research capabilities which are unique in academic institutions. The facility uses a custom designed 1500 watt CO₂ laser (Photon Sources Model 1003) with controls which permit CW, repetitive pulse and shaped power-time cycles. The controls are designed to be interfaced with numerically controlled positioning equipment.

The first experiment station consists of a machine designed for floating zone crystal growth. Four beams will be directed onto the heated region. We will also install anvils for quenching heated molten drops to study new glass and nonequilibrium crystalline compositions. The laser heat source permits high purities, freedom to select ambient atmosphere, and extremely high melting points. This chamber and optics can also be

used for powder synthesis at rapid rates.

The second experimental station will consist of a large controlled atmosphere chamber with provisions for manipulating sample position. It will be used for a variety of cutting, welding, alloying, glazing, and heat treatment experiments. It can also be used for laser chemistry experiments.

FLUID FLOW IN CRYSTALLIZATION PROCESSES

Professor Robert A. Brown is working with three graduate students (C. J. Chang, G. Harriott, and H. M. Ettouney) on a broad research program directed towards a fundamental understanding of the interactions of heat, mass, and momentum transfer in the floating zone method for growing single-crystals from the melt. The techniques for analysis and the physical insights developed in this research have broad application to other processes for growing single-crystal solids. Applications to the Edge-Defined Film Growth process for growing sheets of solid silicon and to the Bridgman process have begun.

During the first year of NASA support three research projects have been initiated, each dealing with a specific aspect of melt crystal growth important in the floating zone process. In each project a combination of analytical modeling and computer-aided calculation is being used to develop both a qualitative understanding of the relevant physics and a quantitative model for separate aspects of the crystal growth process. Our plan is to integrate these individual studies into a detailed description of the floating zone experiment that is being designed by A. D. Little for use aboard the Space Shuttle.

The three research projects are:

- o The effect of heat transfer on melt/solid interface shape.
- o Steady and oscillatory buoyancy-driven convection in melt-growth systems and its effect on solute transfer in melt crystal growth.

- o The coupling between rotationally-driven convection, surface-tension-driven convection, and solute transfer in the floating-zone process at low gravity.

Each of these projects appears as a discrete topic in the research plan of the original proposal to NASA.

Based on preliminary solidification experiments in a vertical Bridgman configuration Professor August F. Witt is currently designing and building a new vertical crystal growth system. This project combines a theoretical heat transfer analysis and an experimental determination of solidification isotherm position and relocation under changing growth conditions. To optimize the systems design, an interactive program is also underway where collected experimental data is used by Professor W. Rohsenow (Mechanical Engineering Department) to refine heat transfer calculations.

Electrodeposition, as in electroplating, electrorefining, and electrowinning is a materials processing area that has important and growing industrial applications. Due to changing energy and environmental considerations, electrodeposition technology will assume growing importance. This is an area, however, that has been little funded and little studied, especially in recent years.

An important new laboratory has been initiated as part of the Materials Processing Center, under the direction of Professor Donald R. Sadoway to study electroprocessing of metals. Initial work is on electroprocessing in molten salts, with emphasis on effect of fluid flow on structure and chemistry of deposit. Equipment has been assembled, and experiments begun by Professor Sadoway, with A. Abdelmassih, D. S. Wilson and P. T. Rogers.

Solid electrodeposits from molten salts are typically incoherent, powdery and/or dendritic. To understand better the

electrodeposition process, fluid flow patterns in the electrolyte will be observed in order to determine how mass transport affects the morphology of the metal deposit. Studies will be conducted both in aqueous electrolytes in which coherent solid electrodeposits are produced as well as transparent molten salt electrolytes. Process variables such as current density and composition of the electrolyte will be adjusted to change the morphology of the electrodeposit and, thus, to permit the study of the nature of electrolyte flow in relation to the quality of the electrodeposit. The results of this work will be helpful in electrochemical cell design and will serve as a data base for subsequent mathematical modelling of fluid flow in such systems.

A fluid flow program of considerable engineering significance is being conducted by Professor David Roylance with three graduate students (G. Frecaut, M. Hvatum and D. Gollob). This work is in the important area of flow behavior in polymer melt processing operations. The ultimate aim of the work is to develop an economical, easily implemented, tool which will allow the polymer processing engineer to predict the influence of fabrication variables on final part quality, and to design fabrication equipment capable of producing optimal parts with a minimum of equipment and energy expense.

This project has been concerned primarily with the application of finite-element computer analysis to polymer flows of the type encountered in melt processing operations. The finite-element method is well suited to a wide variety of problem types, and is able to incorporate irregular boundary conditions and complicated fluid properties more expeditiously than alternative methods. Our code is able to generate values of fluid velocity, pressure, and shear stress at any point within the flow field. As such, it is of value in diagnosing such processing problems as regions of fluid

stagnation at which thermal degradation may occur, or regions of excessive shear deformation which lead to thermomechanical damage. It is further able to generate predictions of the forces which must be applied to the melt to achieve the desired flow, and this information is of value in designing processing equipment of optimal efficiency and minimum energy consumption. Ultimately, the project seeks to have developed a versatile and easily implemented analytical tool which may be used routinely by processing engineers, as well as by researchers in rheology seeking solutions to presently intractable problems.

An important secondary goal is the verification of the computer analysis by application to real problems in polymer processing, so that the method may be placed correctly in the context of alternative theoretical approaches which have been used previously.

ADAPTIVE MATERIALS PROCESSING

This first year of work has been exploratory in nature, examining the potential for computer, and robot applications in materials processing, and for adaptations of materials processing itself through utilization of these new technologies.

Specific processes which have been under consideration are those that produce secondary metal shapes; specifically forging, casting, extrusion, and powder metallurgy.

The approach taken by R. Lund and co-worker, D. Pinsky, has been to arrange a series of three meetings of experts from government, industry, and academia and to report on the conclusions reached by the participants in these meetings. The first meeting, which was held on January 22-24 of this year at MIT's Endicott House, examined the state-of-the-art

in the four process areas and in related technologies (robotics, computers, sensing and control). It also identified problem areas requiring attention if advanced technological solutions were to be attempted. The meeting was attended by 22 people, with a good mix of industrial and academic experts.

A second, follow-up workshop, held on May 4-6, was also at Endicott House. The theme of this meeting was what might be done to create more efficient, more productive metals processing systems. The third meeting, held in late summer, examined the results of our previous deliberations and recommended programs needed to effect radical new metals processing technology.

Abstracts of these conferences and their recommendations are enclosed within this report and more detailed summaries are given in three reports published separately.

III. MATERIALS PROCESSING RESEARCH BASE - DETAILED ABSTRACTS

INTRODUCTION

This section comprises detailed research abstracts of the programs comprising the NASA sponsored Materials Processing Research Base. These are as follows. In each case the program is preceded by the name of the principal investigator or investigators.

NUCLEATION AND RAPID SOLIDIFICATION

1. N. J. Grant, "The Structure and Properties of Rapidly Solidified High Alloy Aluminum Materials."
2. F. J. McGarry, "Rapid Solidification of Polymers."
3. M. C. Flemings and J. Szekely, "Convection in Grain Refining."
4. J. S. Haggerty, "Laser Materials Processing Facility."

FLUID FLOW IN CRYSTALLIZATION PROCESSES

1. R. A. Brown, "Fluid Flow in Crystal Growth: Analysis of the Floating Zone Process."
2. A. F. Witt, "Heat Flow Control and Segregation in Directional Solidification."
3. D. R. Sadoway, "Studies of Materials Electroprocessing in Molten Salts."
4. D. Roylance, "Numerical Modeling and Optimization for Polymer Melt Processing Operations."

ADAPTIVE MATERIALS PROCESSING

1. R. Lund, "Workshops in Adaptive Materials Processing."

NUCLEATION AND RAPID SOLIDIFICATION

PROJECT 1: THE STRUCTURE AND PROPERTIES OF RAPIDLY SOLIDIFIED HIGH ALLOY ALUMINUM MATERIALS

Principal Investigator: N. J. Grant

Personnel: Mr. S. Kang
Mr. W. Wang

RESEARCH ABSTRACT

Using our ultrasonic gas atomization process for producing fine spherical powders of aluminum alloys, solidification rates of 10^4 to 10^5 °K/s were achieved, with over 90 percent yield of minus 250 micron diameter powders. The dendrite arm spacings for the 1 to 250 micron powders varied from about 0.5 to 5 microns, confirming the above solidification rates. Both X2020 and 2024 + Li were produced. The powders were gravity packed into aluminum cans, welded, heated and evacuated, and then hot extruded at a reduction of area of 30 to 1. Excellent properties were obtained with both classes of alloys. One of the X2020 alloys developed ultimate tensile strength values in excess of 90,000 psi with useful ductility.

RESEARCH SUMMARY

1. "Studies of Rapidly Solidified X2020 Alloys," S. Kang

Three alloy compositions were chosen for the current research program: Table 1. The alloys have similar compositions except that the copper-titanium ratios are varied; this is being done to determine the effect on the compositions of the phases and their volume fractions.

In order to overcome the severe segregation problem associated with slowly cooled Al-Li ingot alloys, rapid solidification process via the ultrasonic gas atomization method has been used for powder production. The noted alloys are

TABLE I
Alloy Designation and Compositions of As-received
X2020 Aluminum Master Remelt Alloys

Alloy Designation	Cu	Li	Mn	Cd	Mg	Zn	Fe	Si	Al
(in weight percent)									
2020-68	4.61	1.42	0.50	0.21	0.01	0.02	0.10	0.04	bal
2020-69	4.32	1.88	0.50	0.22	0.01	0.02	0.11	0.04	bal
2020-70	3.60	3.03	0.49	0.25	0.01	0.02	0.10	0.06	bal

available in the form of extruded bars (0.5 x 1.5 inch cross section) after powder production and hot extrusion.

Determination of the physical and mechanical properties of these three alloys is in progress. Total evaluation of the physical properties will include density and modulus measurements. Those measurements were done for 2020-68 and 2020-69 using Archimedes' principle and an ultrasonic (10 MHz) pulse-superposition technique, respectively. Evaluation of the mechanical properties will consist of room temperature tensile, notch-tensile, fatigue and compact-tension tests. Some stress-rupture tests will be performed at intermediate temperature (200°C). The results obtained so far are listed in Table 2. Higher specific modulus and strength values than those of I/M 2024 and I/M 7075 were obtained. Also, it is to be noted that big improvements in strength and elongation values were obtained for the P/M 2020 alloy compared to the I/M 2020 alloy. However, lower fracture toughness values and faster fatigue crack growth rates than those of I/M 2020 are being observed. These are attributed to small grain size, high dislocation density and crack morphology of rapidly solidified P/M materials. Much more work needs to be done to solve the fracture toughness issue, using various thermomechanical treatments and heat treatments. The evaluation of mechanical properties for the first two alloys (2020-68, -69) is close to being finished; tests are underway on the third alloy.

In order to understand the microstructural features of these alloys and to determine the correlation of the structure with properties, extensive transmission electron microscopy (TEM) will be performed. Also, the effects of the different copper lithium ratios on the mechanical properties will be determined.

TABLE II

Physical and Mechanical Properties of High Strength Aluminum Alloys

Alloy	Modulus (psix10⁶)	Density (g/cm³)	UTS (ksi)	YS (ksi)	Elong. (%)	RA (%)	NTS/YS
P/M 2020-68 T6 (1 wgt % Li)	11.3	2.677	89.4	82.2	8.9	14.7	0.73
P/M 2020-69 T7 (1.5 wgt % Li)	11.4	2.623	94.3	90.4	5.3	6.3	0.7
I/M 2020-T6 (1.3 wgt % Li)	11.2	2.713	84.0	77.0	3.0	-	-
I/M 2024-T4	10.6	2.768	72.7	51.0	24.0	23.5	-
I/M 7075-T6	10.4	2.796	83.0	73.0	11.0	-	-

2. "Studies of Rapidly Solidified 2020-Li Alloys," W. Wang

Three alloys (2024-72, 2024-32, 2024-31) were ultrasonically atomized by argon gas and extruded with an area reduction ratio of 30:1. The fourth alloy (49535) was atomized by helium gas. The compositions are shown in Table 3. He-quenched powders indicate a higher average cooling rate by about one order of magnitude compared with that of Ar-quenched powders.

Alloy 2024-72 shows the levels of yield and ultimate tensile strength under the T8 condition. The resultant ductility values are only average. The lower than desired ductility is due both to the high copper content and to overheating of the powders (to 500°C) prior to hot extrusion (see Table 4). The grain size is typically 3-4 microns, but the delta AlLi intermetallic phase is quite coarse due to the overheat problems.

Alloy 2024-32 shows improved mechanical properties over the No. 72 alloy, particularly with respect to ductility at fracture. The highest yield strength was 71.1 ksi; the corresponding ductility of 4.8% is, however, low. In these alloys, to meet a minimum 7 percent ductility requirement, the yield strength must be on the low side. For the T8 condition (495°C x 0.5 hr. + W.Q. + 2.3% C.R. + 190°C x 24 hr. + W.Q) test results show: $\sigma_{YS} = 63.4$ ksi, $\sigma_{U.T.S} = 69.9$ ksi, $el = 7.7\%$ and $R.A. = 12.5\%$ (see Table 5).

The roles of extrusion ratio (from 8:1 to 30:1 area); shape of the extrusion cross-section (round versus rectangular and the ratio of width to thickness for the rectangular section); and intermediate small amounts of cold work are of interest in terms of their effects on subsequent strength and ductility. These processing variables are currently under study.

PUBLICATIONS

1. N. J. Grant, S. Kang and W. Wang, "Structure and Properties of Rapidly Solidified 2000 Series Al-Li Alloys." Presented at the First International Aluminum-Lithium Conference, Stone Mountain, Georgia, May 12-21, 1980. Proceedings of this Conference are to be published in the Fall of 1980.

TABLE III
Compositions of 2024-Lithium Alloys

Alloy	Composition									
	Cu	Mg	Li	Mn	Cd	Fe	Si	Zn	Cr	Al
2024-72	5.92	1.57	1.29	0.36	0.13	0.18	0.06	0.02	-	bal
2024-32	3.96	1.57	2.17	-	-	0.1	0.05	0.02	-	bal
2024-31	4.00	1.92	1.25	0.5	0.24	0.1	0.06	0.02	-	bal
49535	0.03	5.84	1.88	-	-	0.09	0.05	0.03	0.27	bal

TABLE IV
Mechanical Properties of 2024-72

Alloy 2024-72: Al-5.92 Cu-1.57 Mg-1.29 Li-0.36 Mn

TMT	Solution Temp. (°C)	Solution Time (min)	Cold Reduc- tion (%)	Aging Temp. (°C)	Aging Time (hr)	YS (ksi)	UTS (ksi)	Elong. (%)	RA (%)
	495	30.	2.1	190	9	62.0	68.2	5.7	5
	495	30.	3.0	190	9	67.2	70.8	5.3	5
TMT	495*	60.	3.4	190	9	69.6	73.2	5.5	5
	495	60.	10.7	190	9	68.9	71.7	4.6	5
	510	60.	3	190	9	72.1	76.3	5.4	10

*Single test.

TABLE V
Mechanical Properties of 2024-32

Alloy 2024-32: Al-3.96 Cu-2.17 Li-1.57 Mg

TMT	Solution Temp. (°C)	Solution Time (min)	Cold Reduction (%)	Aging Temp. (°C)	Aging Time (hr)	YS (ksi)	UTS (ksi)	Elong. (%)	RA (%)
T4	480	60	-	RT	>22 days	56.7	72.4	10.5	13.3
T4	495	60	-	RT	>12 days	55.4	70.4	8.3	8.3
Notched T + T4	495	60	-	RT	>16 days	$\sigma_N^* = 75.4$	$\frac{\sigma_N}{\sigma_{Y.S.}} = 1.4$	$\frac{\sigma_N}{U.T.S.} = 1.1$	
HR (47%) + T6	480	60	-	120	292	60.9	69.5	7.4	5
T6	495	60	-	190	24	57.6	70.0	8.3	10
T6	510	30	-	190	24	64.7	75.9	6.4	5
T8	480	60	14.3	190	9	66.0	69.7	6.9	10
T8	480	60	2.9	190	24	61.0	66.6	6.2	10
T8	495	60	10.1	190	9	70.4	74.0	4.7	7.5

* σ_N is notched tensile strength.

TABLE V (cont'd)

TMT	Solution Temp. (°C)	Solution Time (min)	Cold Reduction (%)	Aging Temp. (°C)	Aging Time (hr)	YS (ksi)	UTS (ksi)	Elong. (%)	RA (%)
T8	495	60	3.8	190	24	69.2	74.1	6.2	10
T8	495	30	2.3	190	24	63.4	69.9	7.7	12.5
T8	495	30	3.4	190	24	66.0	71.3	6.3	10
T8	510	30	2.3	190	24	69.9	75.3	5.2	5
T8	510	60	2.3	190	24	71.1	76.6	4.8	5
T8	510	60	2.9	190	24	69.6	74.4	4.7	3.3

PROJECT 2: RAPID QUENCHING EFFECTS IN GLASSY POLYMERS

Principal Investigator: F. J. McGarry

Personnel: J. F. Mandell

A. Agrawal

H. D. Lee

RESEARCH ABSTRACT

Density changes in 50×10^{-4} cm. thick films of polystyrene (P.S.) and polyvinyl chloride (P.V.C.) due to rapid quenching from above the glass transition temperatures have been observed, using a specially constructed microbalance. Changes of $\pm 0.0001 \text{g/cm}^3$ can be measured. The more severe the quench, the greater is the departure from equilibrium density: the greater is the free volume content. Residual stresses appear to be absent. Tensile creep, relaxation and stress-strain to failure all reflect free volume content. At room temperature, aging, or densification takes place as a linear function of (log) time. In PVC, the equilibrium is reached after about 3 hours.

I. INTRODUCTION

Metallic glasses prepared by quenching molten alloys at rates approaching 10^6 degrees Centigrade per second have received intensive study (1-7). Such materials possess unusual characteristics:

- 1) They are amorphous rather than polycrystalline.
- 2) The modulus of elasticity is 0.7-0.8 that of the conventional material.
- 3) Exceptionally high flow stress and strength values can be achieved.
- 4) Work hardening is absent, or minimal, and fatigue resistance is superior.
- 5) Isotropic responses to magnetic fields occur. Susceptibility can be greater. Electrical resistivity

is increased; the temperature coefficient of resistivity is lower, or even negative.

6. Superior corrosion resistance is acquired.

A number of methods have been devised to achieve the high cooling rates required, and certain procedures, and alloys now combine to produce metallic glasses in commercial quantities. All the methods share two necessary characteristics: i) intimate contact with the cooling surfaces or media, and ii) physically thin sections are used, to maximize the rate of heat removal.

Compared to metals, synthetic high polymers exhibit thermal conductivity values which are three or four orders of magnitude lower. See Table I. Further, the glass transition temperatures of metals is in the range of 500-1000°C while that for polymers is 50-150°C; most polymers will melt above 150-300°C. Therefore, because of their poor conductivity and the narrower temperature gap, similarly high quench rates are not possible with polymers. Offsetting this, however, is the fact that a polymer in the amorphous glassy state approaches its equilibrium condition very slowly and may never fully achieve a true thermodynamic equilibrium (8). In the process, recently termed "physical aging," small but finite increases in density occur, accompanied by changes in macroscopic properties which often are unusual in character and magnitude. This loss of free volume (a concept used to represent the difference between actual and equilibrium densities) affects creep resistance, ductility, mechanical energy absorption under cyclic deformations, effective modulus and some strength properties (9). It has been studied intensively from a scientific perspective but its technological implications have received far less attention. Hence the purpose of this research is to examine the effects of rapid quenching on the mechanical properties of some amorphous glassy polymers. Of particular interest is the potential for cold forming such materials as polystyrene (P.S.) or polyvinyl chloride (P.V.C.) if they have an unusually

Table I

<u>Material</u>	<u>K-Thermal Conductivity</u> (cals/°C-cm-sec)	<u>-Thermal Diffusivity</u> (cm ² /sec)
Low density polyethylene	8×10^{-4}	
High density polyethylene	11.5×10^{-4}	2.24×10^{-3}
Polypropylene	2.3×10^{-4}	6.76×10^{-4}
High Impact polystyrene	3.0×10^{-4}	8.93×10^{-4}
Polyvinyl chloride	3.0×10^{-4}	8.57×10^{-4}
Iron	0.13	0.154
Aluminum	0.38	0.64
Copper	0.92	1.12

large free volume content because of rapid cooling. (The glass transition temperature for polystyrene is $\sim 105^{\circ}\text{C}$ and that for polyvinyl chloride $\sim 85^{\circ}\text{C}$).

II. QUENCHING OF POLYMERS

To achieve the highest cooling rates thin film specimens are used in this work. Prepared either by casting from a solvent or by hot pressing, typically they are in the $10\text{-}50 \times 10^{-4}$ cm. thickness range. Using a simple, idealized analysis, the cooling behavior when quenched in various media is illustrated in Table II. It can be seen that the rates are much lower than with metals; offsetting this is the entangled long chain molecule structure of a polymer which is conducive to the retention of higher entropy levels at slower absolute rates. Thus with experimental rates which are even lower than the idealized ones shown in Table II, significant contents of excess free volume could be expected. The other interesting feature from these data is the insensitivity of the rate to the temperature of the quench medium, which is characteristic of diffusion limited systems: the inability of the polymer to conduct heat rapidly controls the cooling behavior of the material. In terms of experimental procedure this is a simplifying feature, since extremely low temperature quench media are not convenient tools.

The use of thin film specimens has one serious disadvantage: their weight is in the range of $50\text{-}100 \times 10^{-3}$ gms., so to monitor density changes to ± 0.0001 gms/cm.³, a very high sensitivity balance is required. To use the technique of hydrostatic weighing, a microbalance was constructed following the ideas of Madorsky (10). As shown in Figure 1, this employs a fine tungsten wire in the form of a helical spring about 1 meter long; after winding it on a core, the wire was annealed at $400\text{-}500^{\circ}\text{C}$ for 12 hours, to eliminate creep effects. The balance has a sensitivity of $500 \mu\text{g.}$ and a maximum capacity of 100 mg. Using a cathetometer which reads

Table II

Calculated Cooling Behavior of a Polystyrene
Film (50×10^{-4} cm. thick) When Quenched From 300° C.

<u>Time (secs).</u>	Temperature at Center of Film When Quenched in:		
	<u>I</u> <u>Water</u> (20°C)	<u>II</u> <u>Water</u> (0°C)	<u>III</u> <u>Acetone/Dry Ice</u> (-87°C)
7×10^{-5}	300	300	300
2.8×10^{-4}	300	300	300
7×10^{-4}	286	285	281
1.12×10^{-3}	236	231	211
2.8×10^{-3}	154	144	99
4.2×10^{-3}	101	87	25
7×10^{-3}	51	33	-44

Average Cooling Rate	$51^{\circ}\text{C}(\text{case I})$	=	$35,600^{\circ}\text{C/sec}$
For Center of Film	$33^{\circ}\text{C}(\text{Case II})$	=	$38,100^{\circ}\text{C/sec}$
to Reach	$25^{\circ}\text{C}(\text{Case III})$	=	$65,600^{\circ}\text{C/sec}$

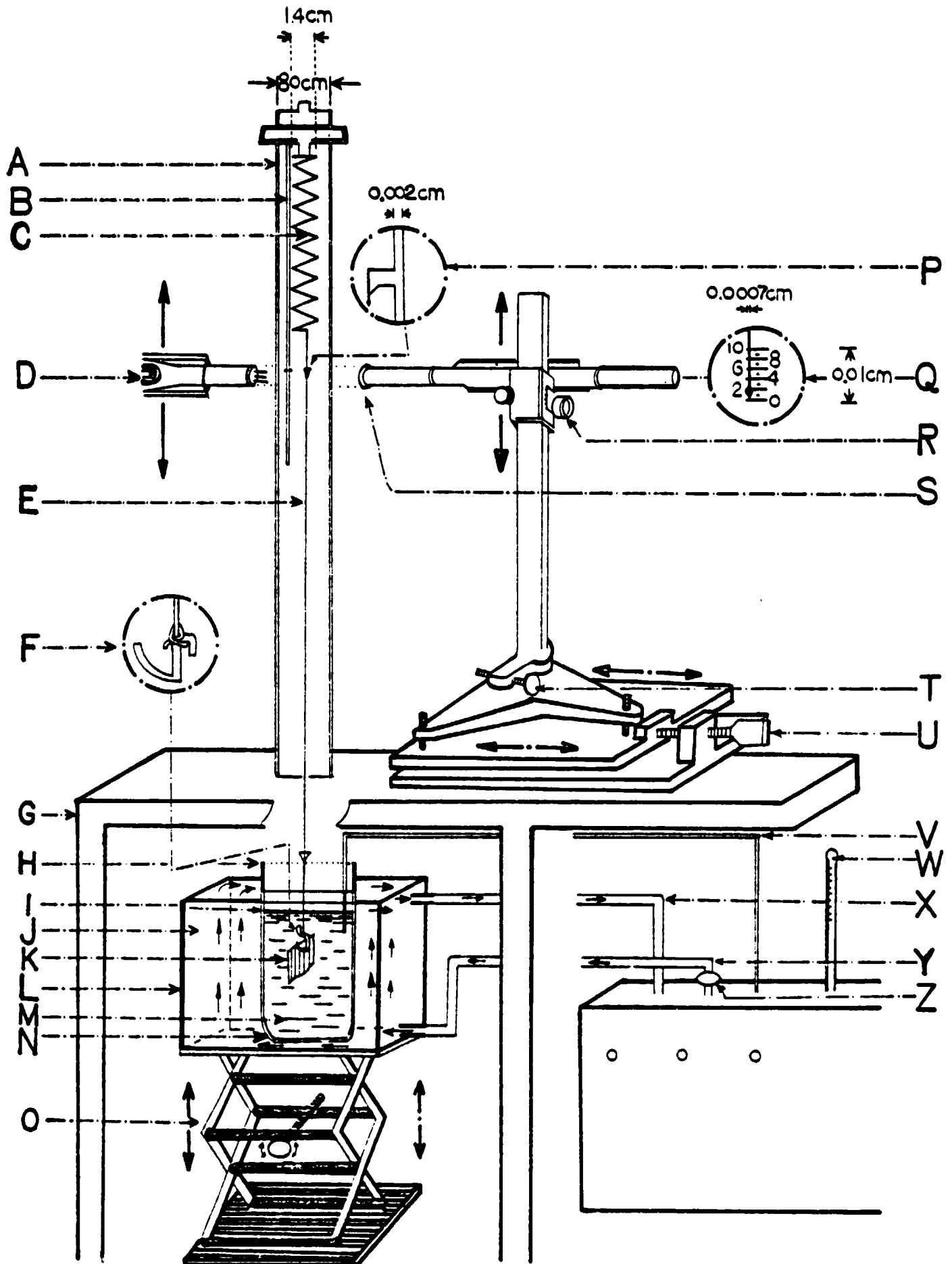


Figure 1

Figures 1/1a. A detailed diagrammatic view of density device and parts.

- A: Pyrex glass tube (80 cm diameter)
- B: Reference scale
- C: Helical spring made of 0.011-cm tungsten wire, or 0.01-cm music wire with 1.4 cm coil diameter
- D: Intense light
- E: Optical fiber (0.002 diameter)
- F: Tungsten-wire-hook tied by optical fiber (no adhesive)
- G: Closed system to prevent air flow
- H: Constant depth marker for immersion wire
- I: Immersion liquid level marker
- J: Constant temperature bath
- K: Specimen
- L: Visible container for constant temperature fluid
- M: Immersion liquid (degassed distilled water)
- N: Visible container for immersion liquid
- O: Jack
- P: Coarse target
- Q: Fine target (marker with 0.0007 cm diameter)
- R: Height reading
- S: Light filter
- T: Horizontal angle adjuster
- U: Focus adjuster
- V: Immersion liquid thermocouple
- W: Bath temperature
- X: Constant temperature bath outlet
- Y: Constant temperature bath inlet
- Z: Flow valve

to 10^{-3} cm, the balance can detect weight differences of 5×10^{-6} gms, giving the desired density sensitivity of 0.0001 g/cm^3 . For example, three samples of PVC film cast from a solvent gave the following density figures from three separate measurements, at 20°C .

Sample A-1	1.36710 gms/cm^3
Sample A-2	1.36714 gms/cm^3
Sample A-3	1.36711 gms/cm^3

EXPERIMENTAL WORK

A large number of experiments on PVC have been performed using in some cases specially designed apparatus. These experiments will be described in detail at a later date. These experiments, however, lead to a common conclusion: the free volume content of glassy PVC directly and strongly affect its mechanical properties. It can be altered substantially by quenching the polymer through its glass transition and even the comparatively low cooling rates which can be achieved, estimated to be $500\text{-}750^\circ\text{C}$ per second in this work, produce very large changes in macroscopic behavior.

VI. CONCLUSIONS

To achieve high rates in quenching glassy amorphous polymers through the glass transition region, films of the order of $20 - 50 \times 10^{-4}$ cm thickness are required. These can be cooled at $200 - 700^\circ\text{C}$ per second, orders of magnitude slower than used with metals and alloys. However, even these rates can produce significant changes in polymer density, which reflect different free volume contents. Room temperature properties after quenching are very different from those of slowly cooled samples; creep and relaxation rates are higher, the modulus is lower, yield and cold drawing are enhanced and other effects may exist. Aging at room temperature after quenching permits a loss of free volume to take place over a number of hours.

Because of the small weights of the samples used, several special pieces of apparatus had to be constructed and put into correct operation.

REFERENCES

1. T. R. Ananthataman, C. J. Suryanaryana, Mat. Sci., 6, 1111, 1971
2. H. Warliomont, Technol. 11, 28, 1980.
3. J. J. Gilman, Science 208, 856, 1980.
4. P. Chaudhari, B. C. Giessen, D. Turnbull, Scientific American, p. 98, April 1980.
5. P. Duwez, R. H. Willens, W. Klement, Jr. J. of Appl. Physics, 1136, 31, 1960.
6. H. Jones, "Rapidly Quenched Metals III," Cantor B., ed., 2, Chameleon Press, London, 1978.
7. H. A. Davies, "Rapidly Quenched Metals III," Cantor B., ed., 2, Chameleon Press, London, 1978.
8. R. N. Howard, "Physics of Glassy Polymers," Wiley and Sons (1973).
9. L. C. E. Struick, "Physical Aging in Amorphouse Polymers and Other Materials," Elsevier Sci. Pub. Co. (1978).
10. S. L. Madorsky, Vacuum Microbalance Techniques, Vol. 2, Plenum Press, New York (1962)

PROJECT 3: CONVECTION IN GRAIN REFINING

Co-Principal Investigators: Prof. M. C. Flemings
Prof. J. Szekely

Personnel: Dr. R. Abbaschian
Dr. C. W. Chang
Dr. N. El-Kaddah
Mr. R. Ewasko
Mr. Y. Wu
Mr. R. Zrilic

RESEARCH SUMMARY

The scientific aim of this program is to obtain a better understanding of the relationship between fluid flow phenomena, nucleation, and grain refinement in solidifying metals both in the presence and in the absence of a gravitational field. An ultimate technical aim is to determine ways to achieve significant grain size reductions in hard-to-process melts. The project has been divided into two sub-tasks. The actual grain refining and supercooling experiments are being carried out by Professor M. C. Flemings' group, while the main thrust of the work of Professor Szekely's group is to study the heat and the fluid flow phenomena in these systems.

A. THE MATHEMATICAL AND PHYSICAL MODELLING OF FLUID FLOW IN CONTAINED AND IN CONTAINERLESS MELTS

In containerless processing applications the metallic specimens are positioned by means of an electromagnetic force field. In ground based applications this force field has to be very strong while in space processing applications a much weaker force should be sufficient.

However in either case this force field will generate flow, the quantitative assessment of which is thought to be crucial for the rational interpretation of the measurements.

The work planned has the following important components:

- (i) The computation of the electromagnetic force fields.
- (ii) The computation of the fluid flow fields resulting from the electromagnetic force fields.
- (iii) The verification of the calculations by experimental measurements.
- (iv) The interfacing was initiated in April, 1980 and the work done to date may be summarized as follows:

(i) Computation of the Electromagnetic Force Fields

It was found more cost effective to sub-contract this task to the G.E. Space Science Division, because of their extensive prior experience in this area. The work concerning the calculation of the electromagnetic force field generated in a cylindrically symmetrical system, using any arbitrary solid configuration has been completed and the appropriate programs have been tested at MIT.

Work is currently in progress at G.E. to generate the program appropriate for the calculation of the electromagnetic force field needed to levitate spherical specimens. It is anticipated that this task will have been completed early next year.

(ii) Computation of the Fluid Flow Fields

The computation of the fluid flow fields may again be broken down into two components:

- (a) Calculations pertaining to cylindrical geometry.
- (b) Calculations pertaining to spherical geometry.

The work pertaining to cylindrical geometry has been completed and the program is appropriately interfaced with G.E.'s program for the calculation of the electromagnetic force field. The attached Figures 1 and 2 show sample calculations for the fluid flow fields in cylindrical containers.

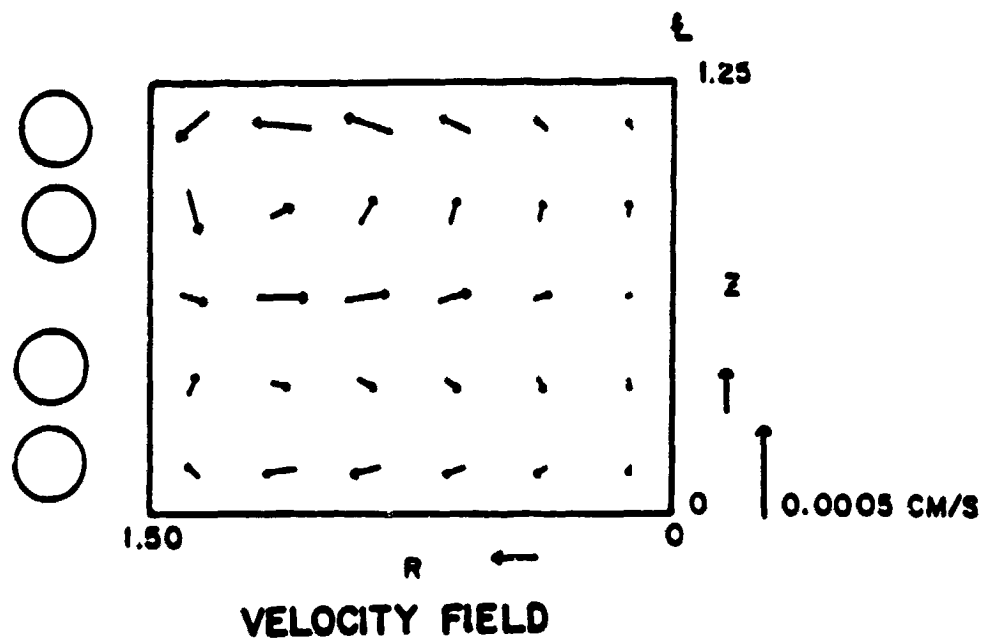


Figure 1. Computed velocity field for molten Al held in a crucible

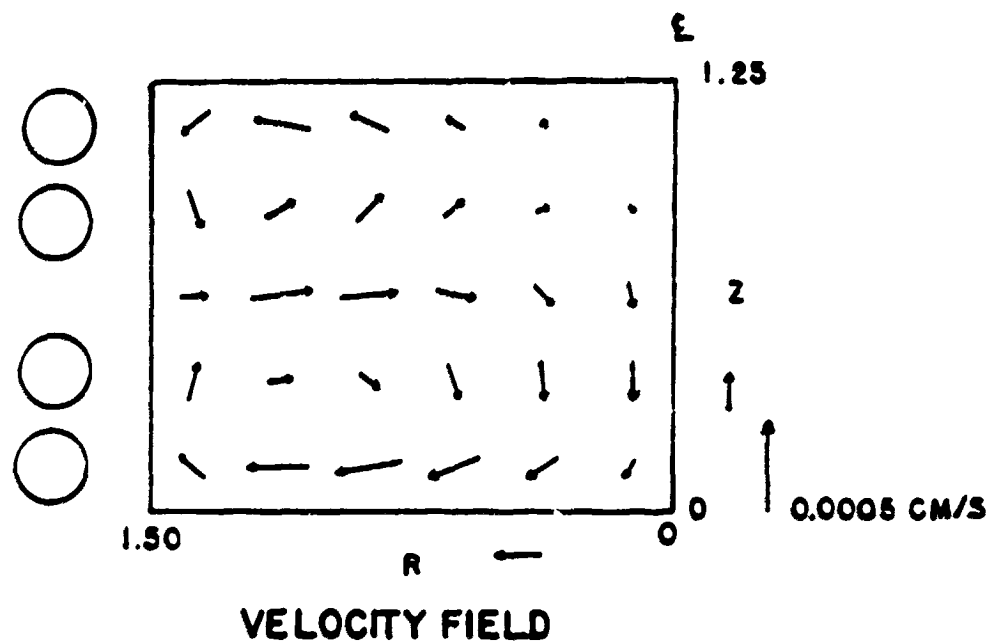


Figure 2. Computed velocity field for the same system but on assuming free boundary condition (levitated drops)

The formulation for spherical geometry has been developed to represent turbulent recirculating flow in the spherical specimen, which is appended to this report. Calculations will be initiated, as soon as the program becomes available from G.E. for the computation of the electromagnetic force field.

(iii) Experimental Program

Regarding the experimental program, an apparatus is currently being designed to enable the verification of the turbulent recirculating flow calculations. It is envisioned that an electromagnetically driven mercury system will be used and that the velocity field will be measured by the use of hot film anemometry.

(iv) Interfacing of the Predictions with the Actual Grain Refining Studies

Until computed results may be generated regarding the behavior of the spherical system, the direct interfacing of the computer results with the grain refining studies would be difficult. However, close contact is being maintained with colleagues in Professor Flemings' group, so that such interfacing should be effected without undue delay.

B. EXPERIMENTAL PROGRAM

Experimental work in this program is aimed at establishing relations between melt supercooling, convection, and dendrite structure (including grain refinement). The bulk of the experimental work to date has been conducted in the apparatus shown schematically in Figure 3, which consists of a levitation melter, temperature measuring and recording system, inoculant feeding unit, and quenching medium. The levitation melter has two reverse turn copper coils which were coupled to a 400 KC, 10 KW high frequency

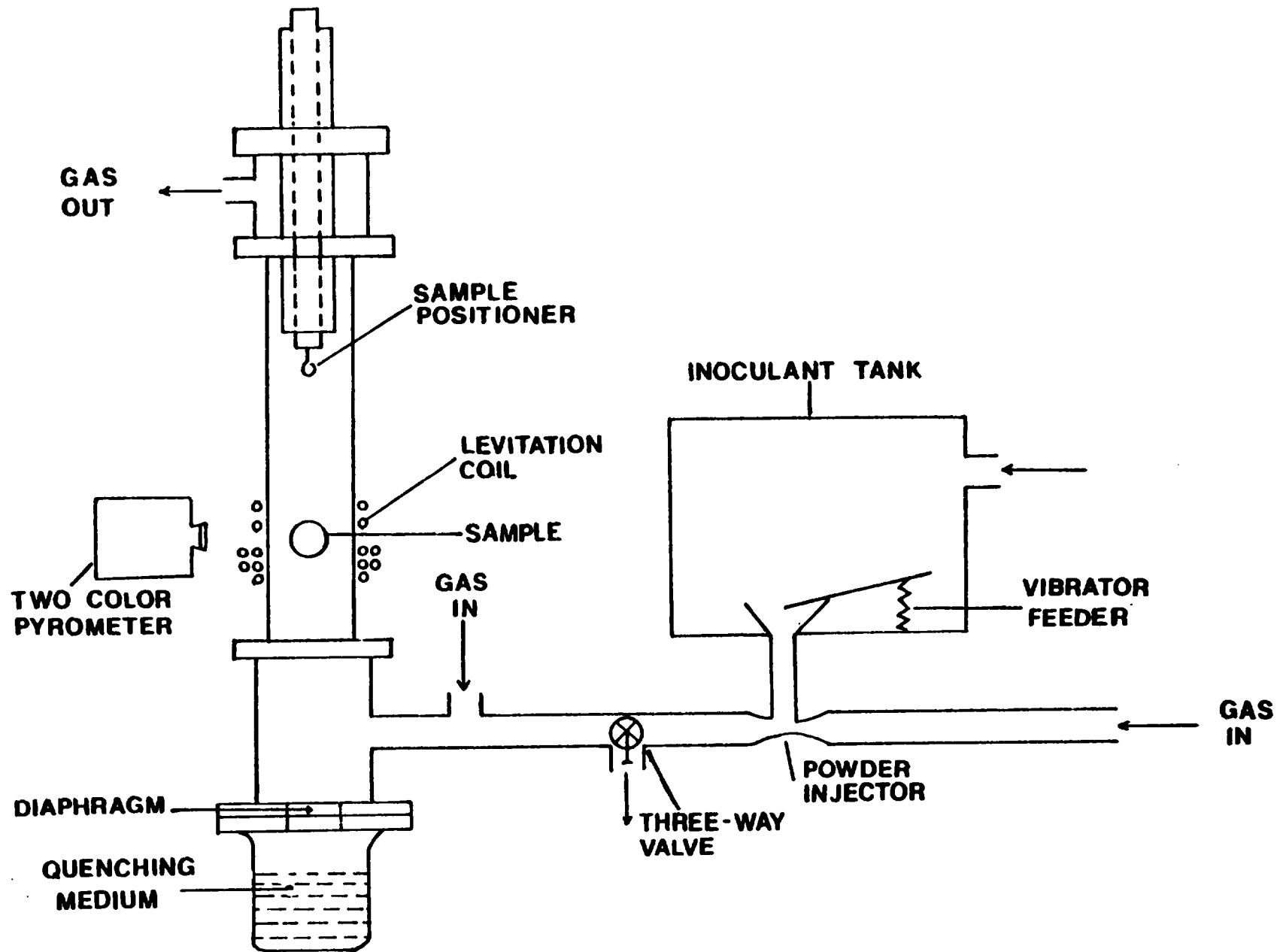


FIGURE 3. SCHEMATIC REPRESENTATION OF THE EXPERIMENTAL APPARATUS

generator. A stream of gas is passed through a glass tube inserted inside the coil. The gases, consisting of He, HE + 2% H, and/or Ar, prevent oxidation of the sample and control the temperature.

The temperature of the levitated sample was measured by a two-color pyrometer and was continuously recorded. The pyrometer, manufactured by Millitron Company, has a built-in calibration unit. The melting point of each levitated sample, however, was used as a reference point to calculate the supercooling or superheating of that sample.

The inoculant feeding unit consists of a vibrator feeder placed inside a sealed tank, through which argon gas with positive pressure is continuously passed. The vibrator feeds the inoculating powder into a funnel, which directs the particles into an injector. Here the particles are accelerated as they pass through a venturi type nozzle. The gas-borne particles are then directed to the levitation chamber or to the exhaust, as desired, via a three-way valve.

Alloys studied thus far are Fe-25% Ni with minor additions of other elements, Table 1, primarily to reduce or eliminate solid state grain growth.

EXPERIMENTAL RESULTS

Supercoolings up to 270°C have been obtained and summary results to date are as follows:

1. A dendritic morphology with relatively coarse grain structure (typically between 100 and 1000 μm) is obtained for superheated samples and for samples undercooled less than 170°C.
2. Some samples initially undercooled less than 170°C and all samples undercooled greater than 170°C possess a spherical "non-dendritic" morphology with an "element spacing", or grain size in the range of 10 to 50 μm depending on initial

TABLE I
Nominal Composition of the Alloys

Designation	Composition
A	Fe-25 pct Ni
B	Fe-25 pct Ni-0.5 pct S
C	Fe-25 pct Ni-1 pct S
D	Fe-25 pct Ni-0.5 pct Nb
E	Fe-25 pct Ni-1 pct Nb
E	Fe-25 pct Ni-0.5 pct Ti
F	Fe-25 pct Ni-1 pct Ti
G	Fe-25 pct Ni-0.5 pct V
H	Fe-25 pct Ni-1 pct V

undercooling and cooling rate after nucleation.

3. Undercooled samples show unusual segregation behavior, including solute rich cores, and solute rich islands, the latter of which may form from remelting during recalescence.

CURRENT WORK

In current work we are analyzing and correlating results obtained to date, and performing heat flow calculations to estimate cooling rates and calculate metal-quench media heat transfer rates. Experiments are being initiated on a nickel-tin eutectic type alloy and in a Perepezko-type apparatus on lower melting point alloys.

PUBLICATIONS

1. J. Grevet, J. Szekely and N. El-Kaddah, "An Experimental and Analytical Study of Gas Bubble Driven Circulation Systems," submitted to Int. J. Heat Mass Transfer.
2. M. Choudhary and J. Szekely, "The Effect of Temperature Dependent Electrical Conductivity on Flow and Temperature Fields in Slags in ESR Systems," submitted to Met. Trans.

APPENDIX

The governing equations for the flow field for spherical drops take the following form:

Continuity equation

$$\frac{1}{r^2} \frac{\partial}{\partial \theta} (\rho r^2 v_r) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (\rho v_\theta \sin \theta) = 0 \quad (1)$$

momentum equation

r-direction

$$\begin{aligned} & \frac{1}{r^2} \frac{\partial}{\partial r} (\rho v_r^2 r^2) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (\rho v_r v_\theta \sin \theta) \\ &= - \frac{\partial \rho}{\partial r} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \mu \frac{\partial v_r}{\partial r}) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (\frac{\mu \sin \theta \partial v_r}{r \partial \theta} + S_r) \end{aligned} \quad (2)$$

θ -direction

$$\begin{aligned} & \frac{1}{r^2} \frac{\partial}{\partial r} (\rho v_r v_\theta r^2) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (\rho v_\theta^2 \sin \theta) = - \frac{1}{r} \frac{\partial \rho}{\partial \theta} \\ & \frac{1}{r^2} (r^2 \mu \frac{\partial v_\theta}{\partial r}) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (\mu \frac{\sin \theta}{r} \frac{\partial v_\theta}{\partial \theta}) + S_\theta \end{aligned} \quad (3)$$

where

$$\begin{aligned} S_r &= \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \mu \frac{\partial v_r}{\partial r}) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (\mu \sin \theta \frac{\partial}{\partial r} v_\theta) - 3 \frac{\mu}{r} \frac{\partial v_\theta}{\partial \theta} \\ &- 4 \frac{\mu}{r^2} v_r - 3 \frac{\partial v_\theta \cot \theta}{r^2} + \frac{\rho \theta^2}{r} + g \sin \theta \beta (\Delta T_J) + (J \times B)_r \end{aligned} \quad (4)$$

$$\begin{aligned}
S_\theta = & \frac{1}{r} \frac{\partial}{\partial r} \left(\mu \frac{\partial v_r}{\partial \theta} \right) + 4 \frac{\partial}{r^2} \frac{\partial}{\partial \theta} \left(\mu \frac{\partial \theta}{\partial \theta} \right) - 2 \frac{\mu v_\theta}{r^2 \sin^2 \theta} \\
& - \frac{\rho v_r v_\theta}{4} - g \sin \theta \beta (\Delta T_o) + (J \times B)_\theta
\end{aligned} \tag{5}$$

(1)
(2)
(3)

here the last three components in the source terms are the body force:

- (1) Centrifugal force (r direction) or Coriolis force (θ direction).
- (2) Buoyance force.
- (3) Electromagnetic body force (Lorentz forces)

Energy Equation

$$\begin{aligned}
\frac{1}{r^2} \frac{\partial}{\partial r} (\rho r^2 v_r T) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (\rho v_\theta \sin \theta T) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\mu}{Pr} \frac{\partial T}{\partial r} \right) \\
+ \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left(\frac{\mu \sin \theta}{Pr} \frac{\partial T}{\partial \theta} \right) + (J \cdot J) / \sigma
\end{aligned}$$

The k- ϵ equation needed to define the turbulent viscosity is basically the same as that documented for cartesian and cylindrical coordinates. However, the final form slightly differs as a result of the strain rate tensor.

The boundary conditions are

$$\begin{aligned}
v_r|_R &= 0 \\
\frac{\partial v_\theta}{\partial r}|_R &= 0 \\
\frac{\partial K}{\partial r}|_R &= 0
\end{aligned}$$

$$\left. \frac{\partial \Sigma}{\partial r} \right|_R = 0$$

$$\left. \frac{\partial}{\partial r} \right|_R = \frac{\rho C_p \mu}{Pr} \Sigma \sigma (T^4 - T_{amb}^4) + \frac{h \rho C_p \mu}{Pr} (T - T_{amb})$$

The computer program for solving these equations has been developed.

PROJECT 4: LASER MATERIALS PROCESSING FACILITY

Principal Investigator: Dr. J. S. Haggerty

STATUS REPORT

The ceramics group within the Materials Processing Center and the Advanced Technology Group in the Energy Laboratory have jointly supported construction of a laser facility which is specifically designed for materials processing research. It gives M.I.T. research capabilities which are unique in academic institutions.

The facility uses a custom designed 1500 watt CO₂ laser (Photon Sources Model 1033) with controls which permit CW, repetitive pulse and shaped power-time cycles. The controls are designed to be interfaced with numerically controlled positioning equipment. The laser is designed to emit 2 600-650 watt Tm₀₀ mode beams, 2 600-650 watt Tm₀₁ mode beams, 1 1200 watt Tm₀₀ mode beam or 1 1500 watt Tm₀₁ mode beam. In all configurations, the laser can be tuned to emit less than 20 watts. This power range will satisfy requirements from smaller diameter crystal growth up to modestly deep penetration welds in steel. The beams go from the laser to the experiment stations through conduits positioned at ceiling level. Removable mirrors are employed to direct the beam(s) to the different experiment stations.

The first experiment station consists of a machine designed for floating zone crystal growth. Four beams are directed onto the heated region. We will also install anvils for quenching molten drops to study new glass and nonequilibrium crystalline compositions. The laser heat source permits high purities, freedom to select ambient atmosphere, and extremely high melting points. This chamber and optics can also be used for powder synthesis at rates which are substantially higher than is possible with the optics and laser (150 watts maximum) we are presently using.

The second experimental station will consist of a large controlled atmosphere chamber with provisions for manipulating sample position. It will be used for a variety of cutting, welding, alloying, glazing, and heat treatment experiments. It can also be used for laser chemistry experiments.

The laser has been delivered, installed and made operational by Photon Sources. It meets or exceeds all performance specifications. The crystal growth station has been constructed and made operational. It is presently undergoing minor modifications.

The funds for the laser heated crystal growth facility came from a combination of four sources, including this NASA grant.

FLUID FLOW IN CRYSTALLIZATION PROCESSES

PROJECT 1: FLUID FLOW IN CRYSTAL GROWTH: ANALYSIS OF THE FLOATING ZONE PROCESS

Principal Investigator: Prof. R. A. Brown

Personnel: Mr. C. J. Chang
Mr. H. M. Ettouney
Mr. G. M. Harriott

SUMMARY

This research program is directed towards a fundamental understanding of the interaction of heat, mass, and momentum transfer in the floating zone method for growing single-crystals from the melt. During the first year of NASA support significant progress has been made on studies of the interaction between heat and mass transfer and melt/solid interface shape in melt growth processes, on the analysis of the fluid mechanics of the floating-zone process, and on the modeling of buoyancy-driven convection in crystal growth from the melt. In the first project, new numerical methods have been developed for calculating melt-solid interface shape in solidification processes. These methods have been adapted to the study of the influence of natural convection on the shape of the melt/solid interface in a prototype of the Bridgman system.

1. SCOPE OF RESEARCH PROGRAM

Our research program is directed towards a fundamental understanding of the interactions of heat, mass, and momentum transfer in the floating zone method for growing single-crystals from the melt. The techniques for analysis and the physical insights developed in this research have broad application to other processes for growing single-crystal solids. Applications to the Edge-Defined Film Growth for growing sheets of solid silicon and to the Bridgman process have begun.

During the first year of NASA support three research projects have been initiated, each dealing with a specific aspect of melt crystal growth important in the floating zone process. In each project a combination of analytical modeling and computer-aided calculation is being used to develop both a qualitative understanding of the relevant physics and a quantitative model for separate aspects of the crystal growth process. Our plan is to integrate these individual studies into a detailed description of the floating zone experiment that is being designed by A. D. Little for use aboard the Space Shuttle.

The three research projects are:

- 1) The effect of heat transfer on melt/solid interface shape.
- 2) Steady and oscillatory buoyancy-driven convection in melt-growth systems and its effect on solute transfer in melt crystal growth.
- 3) The coupling between rotationally-driven convection, surface-tension-driven convection, and solute transfer in the floating-zone process at low gravity.

Each of these projects appears as a discrete topic in the research plan of the original proposal to NASA.

2. RESEARCH SUMMARY

2.1 EFFECT OF HEAT TRANSFER ON MELT/SOLID INTERFACE SHAPE

In principal, the macroscopic shape of the interface separating melt and solid in steady solidification depends on the transfer of heat, mass, and momentum. The conservation statements for the transport of these quantities through both melt and solid phases and across phase boundaries are mathematically coupled to the location of the melt-solid boundary. In turn, the location of the solidification front is set by local statements of conservation of energy and mass along the phase boundary each written in terms of fluxes

extrapolated from the bulk phases. The goal of this portion of our research has been to develop numerical methods for accurately calculating the shapes of melt/solid interfaces from heat transfer analysis.

For developing numerical techniques we first considered modeling crystal-growth processes where conduction is the dominate mode of heat transfer. This is the case when the melt has a high thermal conductivity and when fluid flow in the melt is small enough that convective transport of heat can be neglected. H. M. Ettouney has developed conduction-dominated models for EFG, Bridgman, and the floating-zone processes. The latter two models are most appropriate for processes being run at low gravity. Ettouney has developed several numerical methods for calculating for these models the temperature fields in both phases and the shape of the melt/solid interface. The algorithms are based on the Galerkin finite-element method and combine accurate polynomial approximations to the temperature fields with explicit representation of the melt/solid interface.

The a priori unknown location of the melt/solid interface introduces nonlinearity into the heat transfer problem and the different finite-element algorithms developed by Ettouney are distinguished by the method used to handle this complication. In one group of techniques the heat transfer problem is transformed to a new domain with fixed boundaries and, because of the transformation, a more complicated nonlinear problem for interface shape and temperature field is solved on this new domain. The temperature field defined on the original domain is recovered by inverting the transformation.

The transformation methods have the advantage that the nonlinearities associated with the unknown interface shape are explicit in the transformed equation set and the finite-element/Galerkin form of these equations is solved efficiently by Newton's method. Using Newton's method makes available

powerful computer-aided methods for studying the sensitivity of the interface shape to changes in parameters (Brown et al., in New Methods in Nonlinear Dynamics, ed. by P. Holmes, SIAM, 1980) and for studying the stability and multiplicity of the interface shape (Brown and Scriven, Phil. Trans. Roy. Soc. 297 51-79 (1980)). These methods are now being applied to a systematic study of the microscopic stability of a planar interface separating melt and solid of a single-component.

A second group of numerical methods solve the original heat transfer problem by adaptively adjusting the location of the melt/solid interface until it is the melting point isotherm and energy transported across the interface is conserved. The advantages and disadvantages of these methods compared to the algorithms that transform the equation set have been laid out in a recent manuscript (2).

Ettouney has demonstrated the power of finite element analysis by a detailed study of the heat transfer in Edge-Defined Film Growth (EFG) (1). This work gives bounds on the validity of the much used one-dimensional heat transfer models (Bell, RCA Review 38, 109-138 (1977); Ciszek, J. Applied Physics 47, 440-442 (1976) and provides a basis for process optimization. Toward this end, Ettouney studied the coupling between heat transfer and the lateral (across the thickness of the sheet) segregation of solute caused by curvature of the melt/solid interface. The solute distribution throughout the melt was calculated by the finite-element method for interface shapes dictated by heat transfer analysis. As detailed in (1), the solute segregation across the crystal sheet may be as large as 20 percent of the average concentration in the crystal, depending on interface shape (heat transfer), growth rate, and the segregation coefficient of the solute. The model for solute transport employed was crude. Only diffusion and convection by a uniform velocity field in the direction of growth were accounted for. When

the melt/solid interface is curved the rearrangement of the velocity field near the interface may change significantly the solute distribution. Cellular convection caused by either buoyancy-driven or surface-tension-driven flows or by nonuniform flow through the die may also alter the segregation results. Surface-tension-driven convection may be important in capillary growth systems. Both mechanisms for convection are being studied in the floating zone system.

Finite element analysis is presently being applied to study heat transfer in the floating-zone system being designed by A. D. Little. The goal of this work is to develop an accurate description of the shape of the melt/solid interface on the heat transfer environment and to supply this information and the methodology for calculation to the other studies; see Sections 1.2-1.3.

Besides the numerical calculations discussed above, asymptotic methods, valid when the melt/solid interface varies but little from a plane, are also being developed for the study of the transport phenomena in melt crystal growth. The asymptotic methods are based on the method of domain perturbations originally put forth by Joseph (Arch. Rat. Mech. Anal. 51, 295-303 (1974)) and offer a systematic algorithm for solving transport problems with a free boundary, i.e. a melt/solid or melt/gas interface. These methods have been tested for EFG and will be detailed in a forthcoming publication (3).

2.2 FLUID MECHANICS OF A ROTATING LIQUID ZONE

Research has focused on understanding the fluid mechanics of a liquid zone trapped between two cylindrical and differentially rotated solid rods and is aimed at describing quantitatively the effect on mass transfer in the melt of rotation of the crystal and feed rods. So far, models of these fluid flows valid only in small regions of the zone and more generally applicable numerical simulations have been initiated. The numerical and analytical results are being compared against

each other and will be confirmed by comparison to experimental results that have been taken on the micro-zone apparatus at A. D. Little.

G. M. Harriott has developed exact analytical expressions for the axisymmetric swirling flow in a rotating liquid drop that is cylindrical in the absence of rotation and that is rotated slowly. Both the streamlines throughout the fluid and the deflection of the liquid/gas interface are calculated explicitly for low rotation rates, measured by the Reynolds number $N_{Re} \equiv R (\Omega/\nu)^{1/2}$.

The axisymmetric flows in a cylindrical drop have also been calculated by finite-element analysis. These calculations account for the three-dimensionality of the velocity field and the effect of surface tension in determining the shape of the gas/liquid interface. The calculations combine the mixed finite element approximation found to be highly efficient by Gresho et al. (Proc. Third International Conference on Finite Elements in Flow Problems, Banff, Canada, 1980) and the methodologies developed by Ettouney and Brown (1) for efficient calculation of the unknown boundary shape, here the gas/liquid meniscus. Both asymptotic and numerical results are being prepared for publication (5).

A related study is focused on explaining the radial vortices observed in the A. D. Little micro-zone apparatus when the top and bottom solid rods are spun in equal counter-rotation (Fowle et al. ADL ref. C-82435, 1980). Under these conditions the zone contains a shear layer about its axial midplane in which the azimuthal velocity changes direction. When the rods are rotated at a velocity such that the Reynolds number $N_{Re} \equiv R (\Omega/\nu)^{1/2}$ is greater than 8.8 elliptical swirls that straddle the midplane appear on the surface of the liquid zone. At Reynolds numbers slightly above 8.8 patterns of two or three vortices were observed spaced evenly about the circumference of the liquid column.

George Harriott has developed a theory that describes the onset of these swirls as due to the onset of wave-like perturbations of the velocity field in the shear layer. An approximate method introduced first by Rayleigh (Proc. Lond. Math Soc. 19 67-74 (1887)) and adapted to rotating flows by Waxman (Astrophysical J. 41 647-667 (1979)) has been applied for the case when the perturbations have small amplitude and are nearly inviscid. The theory gave a critical Rayleigh number of 6.0 in unexpectedly close agreement with the experimental value of 8.8. Subsequent work is being performed to refine the analysis by full numerical solution of the equations for linear stability.

2.3 BUOYANCY-DRIVEN CONVECTION

A third study is into the effects of laminar and oscillatory buoyancy-driven convection on melt/solid interface shape and solute transfer in crystal growth from the melt. The research of C. J. Chang has been directed towards numerical modeling of natural convection in steady solidification. So far, a Galerkin/finite-element method has been developed that calculates velocity, pressure, and temperature fields and melt/solid interface shape by solving the mass and momentum equations in the melt and the energy balances in both phases. The numerical techniques combine the mixed finite element approximation developed by Taylor and Ijam (Comp. Meth. Appl. Mech. Engng. 19 429-446 (1979)) for natural convection with the ISOTHERM technique developed by Ettouney (1) for calculating melt/solid interface shape.

The buoyancy-driven flow calculations were bench-marked against those of other researchers for flow in a square-enclosure with heated sidewalls (without change of phase) and were found to be in complete agreement. Calculations have also been performed for a liquid in a cylindrical cavity with insulated sidewalls and heated from below. In this configuration, convection is initiated only when the Rayleigh number $N_{Ra} = \frac{\beta \Delta g L^3}{\alpha \nu}$ exceeds a critical value that was first calculated

-03-

by Sabi and Charleston (Int. J. Heat Mass Trans. (1970)) for cylinders of varying aspect ratios. Computer-aided methods for detecting multiple steady states have been used to calculate the onset of convection in a cylinder and are being extended to track the evolution of the convective patterns. Other methods are being developed for detecting and tracking the time-periodic or pulsating convective flows that have been observed in low Prandtl number liquids (melts) and that are known to be important in crystal growth processes.

The calculations including solidification have concentrated on a prototype of a directional solidification furnace and are meant to model an experimental system being developed by Wang and Witt in the Material Science Department at M.I.T. The model consists of a cylindrical ampoule with hot and cold ends separated by a nearly adiabatic middle region. Convective flows and melt/solid interface shapes have been calculated as a function of Rayleigh number and dimensionless crystal growth velocity, measured in terms of the Peclet number $Pe = LU/\alpha$ where L is the length of the ampoule and α is the thermal diffusivity of the melt. Steady flows have been calculated for Rayleigh numbers up to 10^6 , near the limit where oscillatory flows have been observed in a similar system (Kim et al., J. Electrochem. Soc. 125 475-480 (1978)). The solute segregation caused by these cellular flow patterns is presently under study.

3. PRESENTATIONS AND PUBLICATIONS

PRESENTATIONS

1. H. M. Ettouney and R. A. Brown, "The Shape of Melt/Solid Interfaces During Steady Solidification." Presented at International Conference on Theoretical and Applied Mechanics, Toronto, August 17-23, 1980.

2. H. M. Ettouney and R. A. Brown, "Melt/Solid Interface Shape and Solute Segregation in Edge-Defined Film Growth," presented at Second Workshop on the Processing of Electronic Materials, Brown University, October 16-17, 1980.
3. H. M. Ettouney and R. A. Brown, "The Calculation of Melt/Solid Interface Shape During Steady Solidification." Presented at the 73rd Annual Meeting of the AIChE, Chicago, November 17-20, 1980. Manuscript available.
4. R. A. Brown and C. J. Chang, "The Effect of Natural Convection on the Shape of Melt/Solid Interface." Presented at the 33rd Annual Meeting of the Fluid Mechanics Division of the American Physical Society, Ithaca, November 24-26, 1980. Abstract published in Bull. Amer. Phys. Soc. 25 1100 (1980).
5. R. A. Brown, "The Mechanics of Hollow Sphere Formation," Materials Processing in Space Symposium, Joint N.W./Rocky Mountain Meeting of the American Chemical Society, Salt Lake City, June 12-14, 1980.

PUBLICATIONS

1. H. M. Ettouney and R. A. Brown, "Finite Element Methods for Steady Solidification Problems." J. Comp. Physics, submitted (1980).
2. H. M. Ettouney and R. A. Brown, Effect of Heat Transfer on Melt/Solid Interface Shape and Solute Segregation in Edge-Defined Film Growth: Finite Element Analysis. J. Crystal Growth, submitted (1980).
3. H. M. Ettouney and R. A. Brown, "Effects of Lateral Heat Transfer on Melt/Solid Interface Shape and Solute Segregation; perturbation analysis. Int. J. Heat Mass Transfer to be submitted (1980).
4. C. J. Chang and R. A. Brown, "Finite Element Calculation of Natural Convection During Steady Solidification. Int. J. Numerical Methods in Fluids, in preparation.
5. G. Harriott and R. A. Brown, "The Fluid Mechanics of a Differentially Rotated Captive Drop." J. Fluid Mech., in preparation.

PROJECT 2: HEAT FLOW CONTROL AND SEGREGATION IN
DIRECTIONAL SOLIDIFICATION

Principal Investigator: Prof. A. F. Witt

Personnel: Prof. W. Rohsenow

Mr. B. Ahern

Mr. C. Herman

Mr. T. Jasinsky

Ms. C. Wang

ABSTRACT

The reported research is directed toward the optimization of crystal growth and segregation during solidification in Bridgeman-type configurations. The first phase of this study was concerned with a determination of the effects of thermal boundary conditions on growth and segregation of doped Germanium in a conventional system. Making use of interface demarcation and spreading resistance analyses, it was found that at constant ampoule lowering rates, both growth and segregation remain non-steady state for growth lengths of up to 6 cm. The rate of growth is significantly less than the lowering rate under high axial thermal gradient conditions ($dT/dx \approx 150^\circ\text{C}/\text{cm}$) but exceeds the lowering rate by to a factor of two (2) at low applied thermal gradients ($dT/dx \approx 60^\circ\text{C}/\text{cm}$). Upon temporary arrest of ampoule lowering uncontrolled growth (ranging from 50 μm to in excess of 2 mm) or back melting takes place depending on the magnitude of the existing axial thermal gradient. With the resumption of ampoule lowering a no-growth condition is observed ranging from about 5 seconds to more than 60 seconds.

The segregation behavior observed is largely unexpected and as yet unexplained. It is found that during temporary arrests (periods of uncontrolled growth) the concentration of incorporated dopant (Ga) increases under conditions of decreasing rate of growth. Concentration maxima (up to 30 percent in

excess of that for steady state growth) are reproducibly observed under a vanishing growth rate, while with the resumption of controlled growth the initial dopant concentration decreases under increasing rate of growth and fails to exhibit the expected value of $C_L k_0$. The observed growth and segregation behavior is currently studied and a manuscript is being prepared for publication.

The growth and segregation data obtained are of theoretical interest, but constitute primarily a data input for a comprehensive thermal modelling approach to the design of a Bridgman type growth system. The objective of currently conducted comprehensive thermal analyses is to obtain a quantification of the effects of furnace - imposed boundary conditions on system design based on the use of coaxial differential heat pipes separated by an (adiabatic) linear thermal gradient region. Thermal characterization of the prototype system and related thermal modelling will now be carried out in cooperation with Professor Brown (Chemical Engineering).

In an independent study a theoretical analysis of the back-melt process associated with seeded growth experiments, is carried out in cooperation with C. E. N. Grenoble. This study indicates that during melting of HgCdTe, for example, the solid phase must be expected to be superheated by up to 85°C. The crystal-melt interface is predicted to be constitutionally stable for a perfect solid state matrix. Break-down phenomena ahead of the interface must however be anticipated for real matrices in which clustered point defects and volume defects constitute nucleation sites for solid-liquid transformation. The implications of these findings for seeded Bridgman type growth of HgCdTe and PbSnTe in a reduced gravity environment are currently under investigation.

RESEARCH SUMMARY

- A. A conventional Bridgeman type growth system was modified to permit current induced crystal-melt interface demarcation during single crystal growth of Ga doped germanium without distortion of the thermal field. A further modification consists in the installation of a cooling system to provide for controllable axial thermal gradients during growth. The quantitative investigation of the growth behavior in this system revealed effects which have significant theoretical and experimental implications. It is found that for the given thermal configuration the establishment of a thermally and compositionally equilibrated solid-melt interface is only possible if low axial ($dT/dx \approx 50^\circ\text{C}/\text{cm}$) thermal gradients are applied. In the presence of steeper gradients uncontrolled growth of length up to $1500\ \mu\text{m}$ is observed during equilibration which has pronounced effects on the initial dopant segregation. Our studies reveal moreover that the location of the crystal-melt interface during growth is subject to continuous change, reflecting a significant difference between the ampoule lowering rate and the microscopic rate of growth. The shift of the growth interface location over a growth distance of 5 cm ranges from $+0.9\ \text{cm}$ (relocation into the hot zone) to $-0.8\ \text{cm}$ (relocation out of the hot zone) depending on the axial thermal gradient along the crystal. This finding confirms the existence of a pronounced "end effect" which is expected to be controllable in the differential heat pipe system currently under construction. Through quantitative microscopic growth rate analyses it is found that no growth takes place for a period of between 50 to 60 sec after initiation of ampoule lowering. For fixed original thermal gradient conditions any arrest of ampoule lowering results in a relocation of the crystal-melt interface, the extent of which is a function of the length of crystal growth and of the duration of the arrest

At a lowering rate of 4 $\mu\text{m}/\text{sec}$ an arrest for 300 sec resulted in uncontrolled growth of 300 μm (after growth of 3 cm) while an arrest of 1800 sec led to back-melting in excess of 400 μm . A study of the crystal-melt interface morphology, through interface demarcation, shows that constant interface curvature ($r = 10 \times \text{crystal radius}$) is achieved after about 2 cm of growth and that further displacements of the interface location with continuing growth do not affect the growth interface morphology. An analysis of the observed radial segregation behavior on the basis of the Sekerka and Coriell theory suggests non-equilibrium behavior with the observed radial composition variation being significantly less than predicted.

The axial segregation behavior of crystals grown differs markedly from that predicted and shows as yet unexplained anomalies presently under investigation. Of primary concern is the observation that during all lowering arrests the dopant concentration in the associated uncontrolled growth regions increases steadily under constant or decreasing rate of growth and reaches maximum values (at a distance of some 20 μm from the regrowth interface) which are a pronounced function of the duration of arrest. The dopant concentration in the first portion grown after resumption of lowering (a region of about 20 μm) decreases under conditions of steadily increasing rate of growth. It is also of interest to note that the dopant concentration after resumption of growth reaches at no time a level lower than that prior to the arrest. This observation suggests the absence of compositional equilibrium during the arrest period of alternately compositional changes in the matrix as a result of solid state diffusion. Lowering arrests can under the given circumstances not be used, as intended, to determine C_L values during growth. The nature of the observed segregation effects and their sensitivity to experimental variables is under investigation.

- B. The primary thrust of thermal analyses in the context of the present research program is to elucidate the effects of thermal boundary conditions on the temperature field in the hot-zone of a Bridgeman-type solidification system. The system currently under construction involves two aligned isothermal regions (differential heat pipes) separated by a gradient region in which one-dimensional heat transfer can be established. The currently conducted thermal analyses are aimed at establishing dimensions for the gradient region as well as at providing input for the structural materials such as heat guiding coaxial tubes and insulation systems to be used. The analyses are moreover concerned with a determination of the effects of crucible materials, translation rates and "end effects" on the thermal field configuration and its stability.

While computer modelling of the two-dimensional heat transfer for crystals in growth configuration is needed (and already in progress) to obtain accurate quantitative solutions regarding the temperature field produced by different sets of boundary conditions useful results have already been obtained from a series of basic thermal analyses. The propagation of radial thermal gradients has been investigated by analytically solving the two-dimensional heat conduction equation for the case of a semi-infinite cylinder (insulated on its perimeter) whose base had an arbitrary temperature profile chosen to accentuate radial gradients. The solution yielded the decrease of initial radial gradients with distance into the insulated zone; no significant gradients are encountered at a distance of 0.5 diameters into the insulated region. The gradient region in the system under construction has therefore been designed to exceed in length the diameter of the tubular cavity.

Presently under development is a two-dimensional finite difference model for the heat conduction in the ampoule

under a wide variety of thermal boundary conditions. After completion it will permit testing of the relationship of axial to radial gradients, of the effect of conduction in the crucible on radial gradients and of the effect of non-perfect insulation. The results will be used to finalize and optimize furnace design.

- C. In cooperation with C.E.N. Grenoble a theoretical analysis of transient and steady state back-melting in a Bridgman type configuration was undertaken. This analysis was made in view of the conclusion reached by Verhoeven et al. that binary systems are during (directional) melting subject to superheating the magnitude of which is controlled by the liquidus-solidus separation. This phenomenon was considered to be of extreme importance in the context of controlled back-melting and regrowth of HgCdTe and PbSnTe (in reduced gravity environment) since the liquidus-solidus separations for the pseudo-binary compositions of interest are 85°C and 15°C respectively. The results of this analysis indicate that the time required to reach steady state melting is $t = 20 D_s / R^2$ (strongly dependent on D_s) and that the width of the diffusion boundary layer in the solid ahead of the phase boundary reaches a value of $3.6 D_s / R$ at steady state. The analysis shows moreover that during transient back-melting the interface temperature changes by ΔT , the separation of the liquidus-solidus and that the same interface temperature change is encountered during transient regrowth. This temperature change has significant implications since it requires that one-dimensional heat flow within the gradient region of a Bridgman-type system must extend at least over a ΔT of 100°C if growth interface planarity, the prerequisite for radial composition uniformity, is to be maintained.

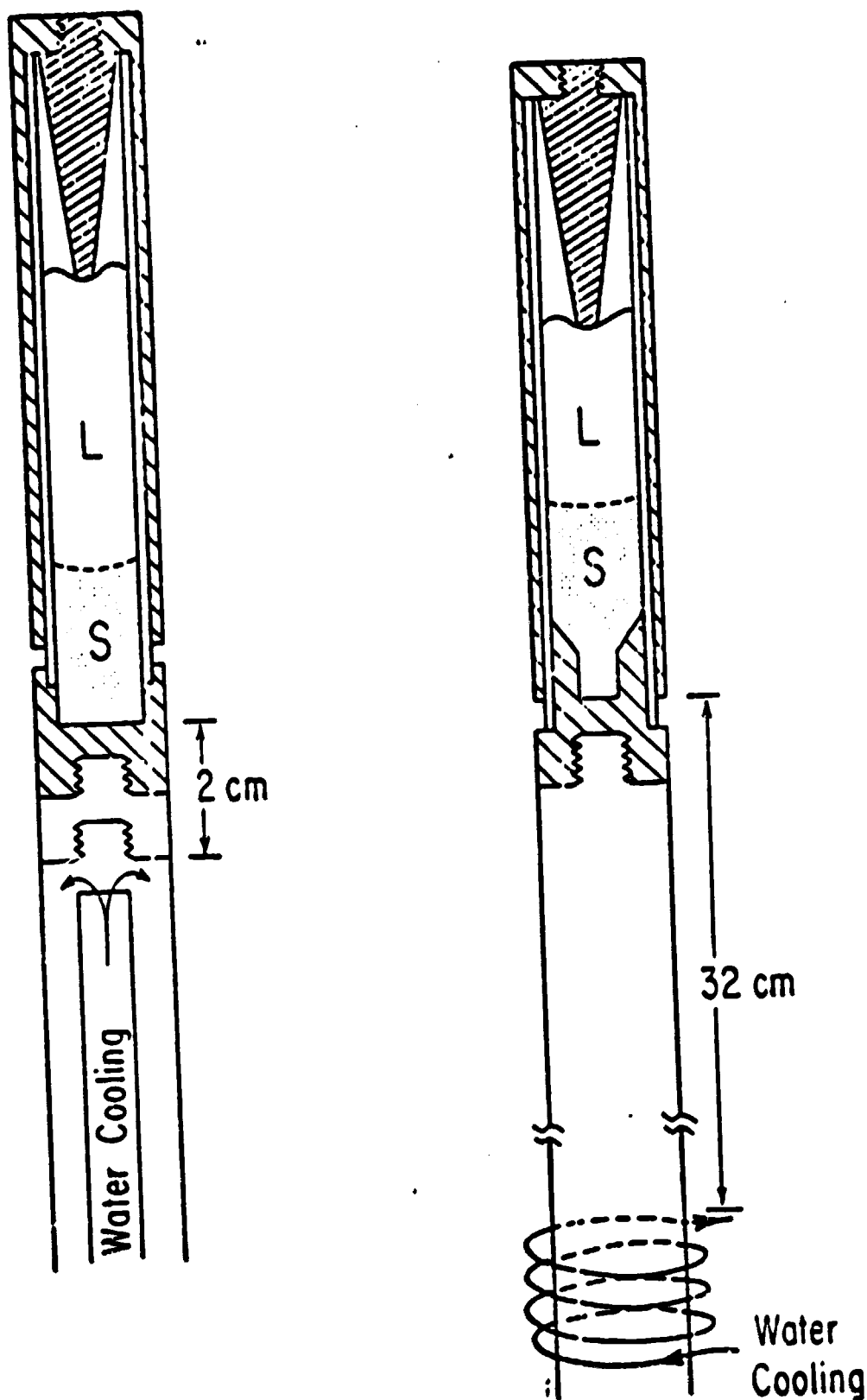


Figure 1. Ampoule configurations and thermal gradient control systems used in Bridgeman growth of Ga doped germanium.

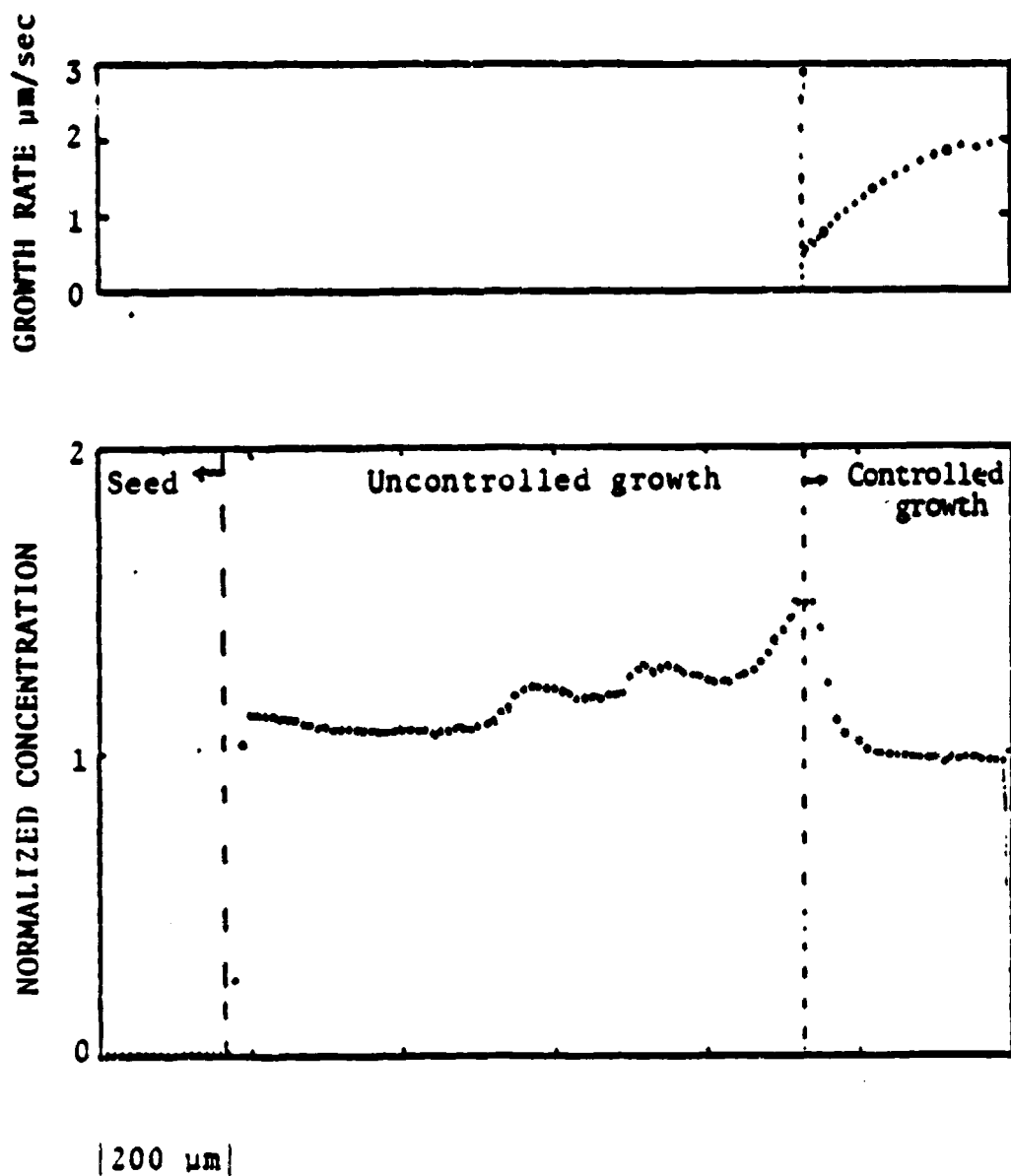


Figure 2. Uncontrolled growth and dopant segregation associated with seeding prior to Bridgeman-type growth; observe the dopant concentration decrease during the initial transient controlled growth.

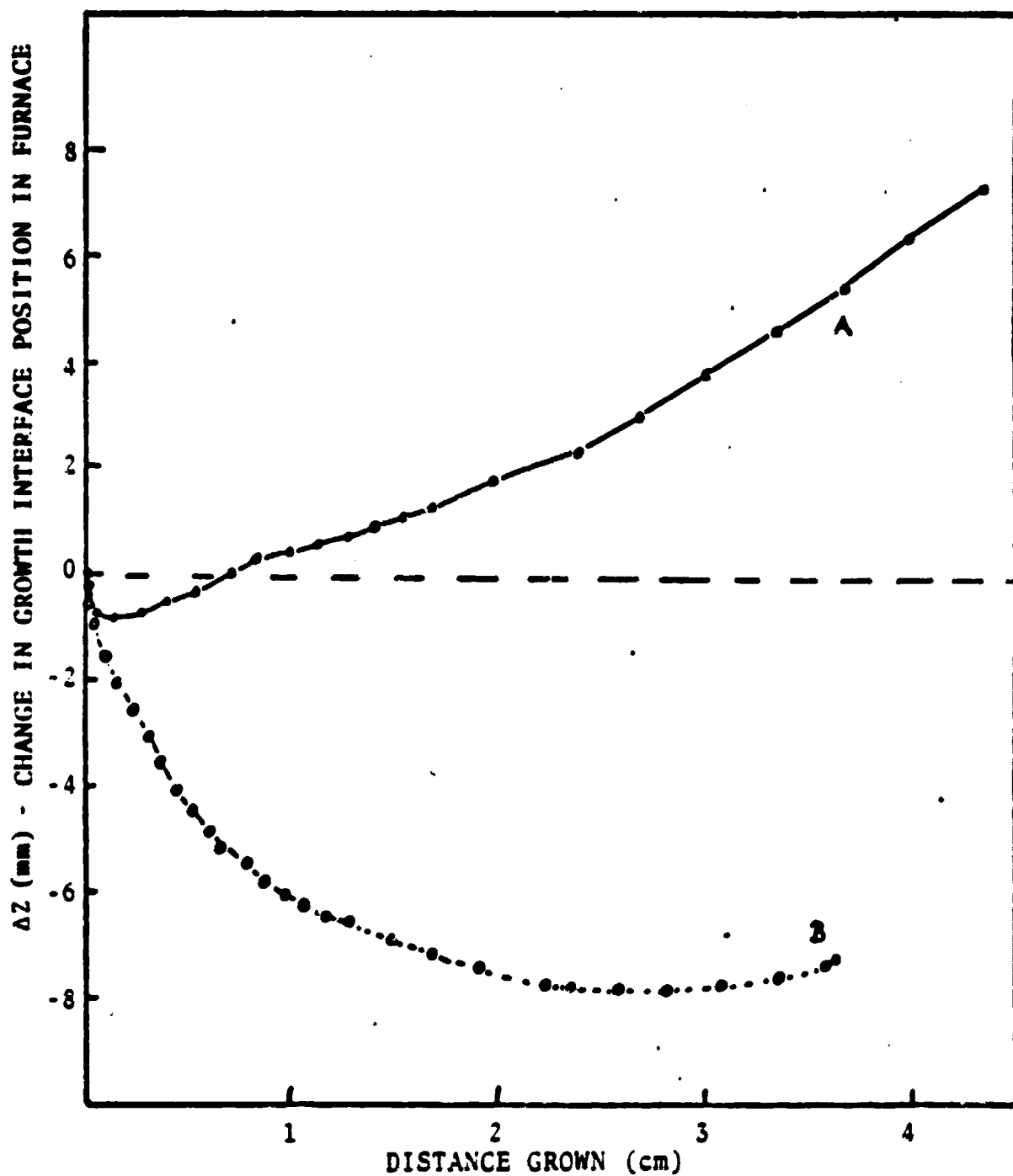


Figure 3. Relocation of crystal-melt interface during growth under high (A) axial thermal gradient and under small (B) axial thermal gradient (see text).

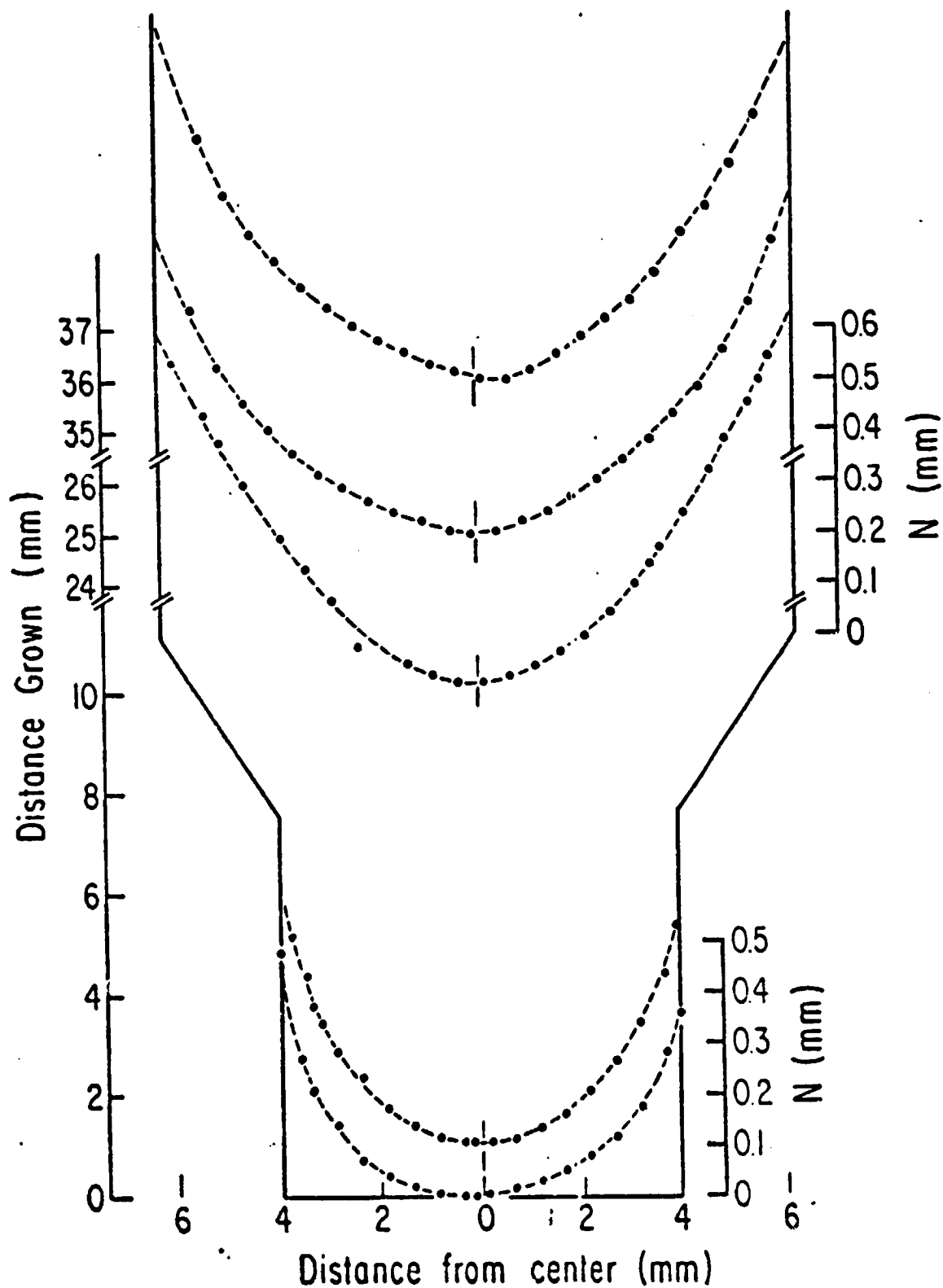


Figure 4. Crystal-melt interface morphology and its change during growth in Bridgman configuration

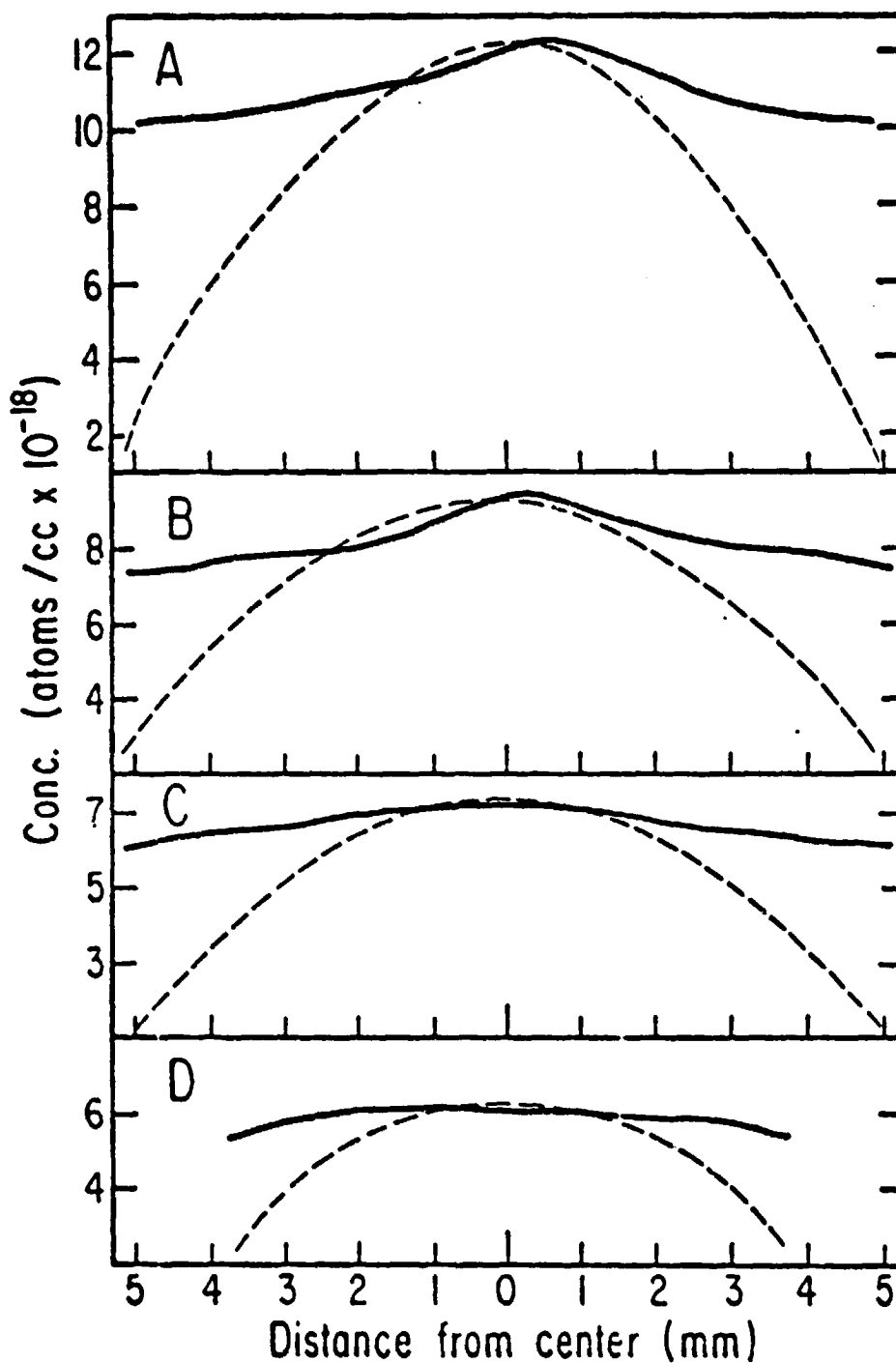


Figure 5. Radial dopant segregation in Ga doped germanium (solid lines) and corresponding theoretical segregation

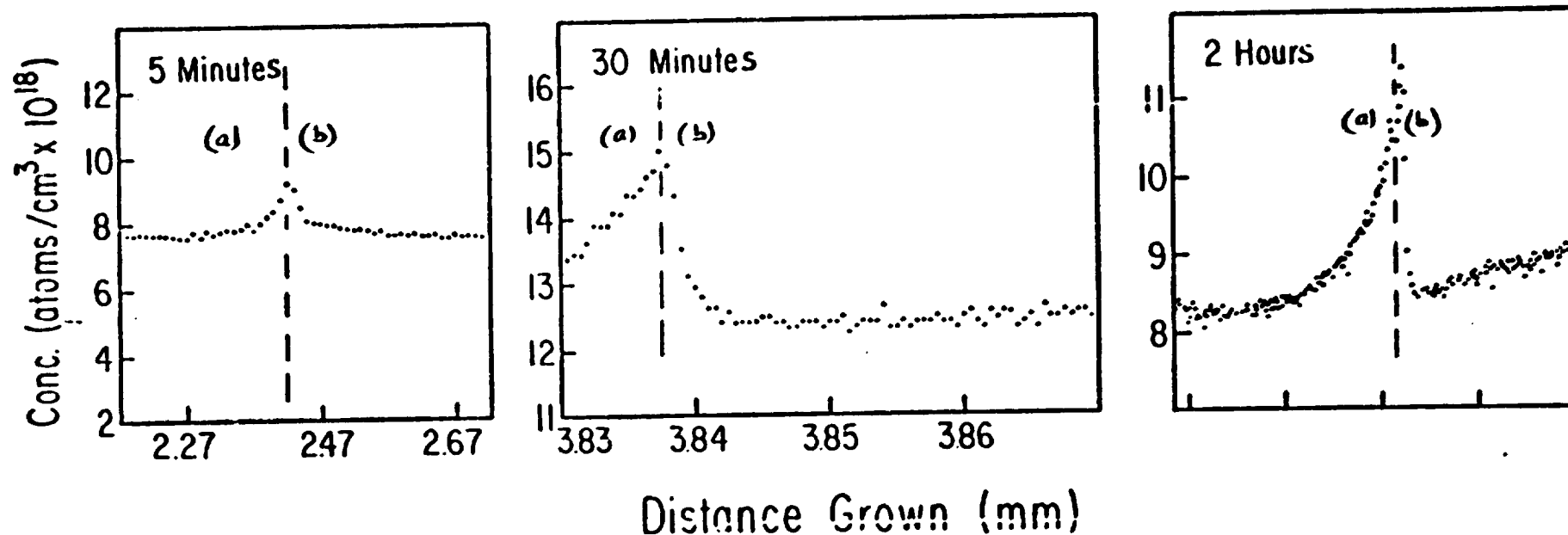


Figure 6. Anomalous segregation during arrest of crucible lowering (a) and during initial transient growth (b) for various times of arrest

PROJECT 3: STUDIES OF METALS ELECTROPROCESSING IN
MOLTEN SALTS

Principal Investigator: Prof. R. Sadoway

Personnel: Mr. A. Abdelmassih

Mr. D. S. Wilson

Mr. P. T. Rogers

RESEARCH ABSTRACT

Molten salts are very important solvent systems in which the electrodeposition of a wide variety of metals may be conducted. However, solid electrodeposits from molten salts are typically incoherent, powdery and/or dendritic. To understand better the electrodeposition process, fluid flow patterns in the electrolyte will be observed in order to determine how mass transport affects the morphology of the metal deposit. Studies will be conducted both in aqueous electrolytes in which coherent solid electrodeposits are produced as well as transparent molten salt electrolytes. Process variables such as current density and composition of the electrolyte will be adjusted to change the morphology of the electrodeposit and, thus, to permit the study of the nature of electrolyte flow in relation to the quality of the electrodeposit. The results of this work will be helpful in electrochemical cell design and will serve as a data base for subsequent mathematical modelling of fluid flow in such systems.

RESEARCH SUMMARY

It is generally true that electrowon metal is of better quality than the thermal reduction product. However, solid electrodeposits from molten salts are typically incoherent, powdery and/or dendritic.

The novelty of the present study is its consideration of the effects of fluid flow of the electrolyte in seeking to explain

the poor quality of solid electrodeposits in molten salts. The plan is to electrodeposit the same metal in separate experiments from aqueous solutions and molten salt electrolytes. Transparent cells will allow observation of electrolyte circulation patterns.

As this project is the first of its kind at the Materials Processing Center, in the first year much time was devoted to building up a laboratory for electroprocessing. The capabilities for electrodepositing metal both from aqueous electrolytes and molten salts have been achieved.

An apparatus for the preparation of anhydrous molten salt electrolytes of adequate purity has been built. The salts are charged into a tube which can be heated to 500°C. A stream of hydrogen chloride, chlorine, and helium gases in controlled ratios passes over and reacts with the salts to remove water and oxy-compounds.

An electrochemical method of analysis to test melt purity has been developed. The technique is based upon the measurement of residual polarographic currents of candidate supporting electrolytes. Ideally, one should measure zero current at voltages below the decomposition voltage of the electrolyte. Current at lower voltages is an indication of the presence of charge bearing impurities which could conceivably be co-deposited during metal electrolysis. The purification schedule has been optimized in response to the results of the polarographic studies.

On a parallel track, a transparent electrolysis cell for electrodeposition studies in aqueous solutions has been built. Plating studies of nickel in Watts bath type electrolytes have begun.

Personal contacts have been established with several people at the Marshall Space Flight Center. In particular, consultations with Robert B. Owen of the Space Sciences Laboratory

have made workers on this project aware of the KC-135 low gravity electrodeposition experiments. We intend to continue to confer with Dr. Owen as we work towards the development of optical techniques for observing and recording the fluid flow behavior of transparent electrolytes. This collaboration may result in the design of some experiments to be performed on board future flights.

PROJECT 4: NUMERICAL MODELING AND OPTIMIZATION FOR POLYMER
MELT PROCESSING OPERATIONS

Principal Investigator: Prof. D. K. Roylance

Personnel: Mr. B. Collins
 Mr. C. Douglas
 Mr. G. Frecaut
 Mr. D. Gollob
 Ms. M. Hvatum

RESEARCH ABSTRACT

This project has been concerned primarily with the application of finite-element computer analysis to polymer flows of the type encountered in melt processing operations. The finite-element method is well suited to a wide variety of problem types, and is able to incorporate irregular boundary conditions and complicated fluid properties more expeditiously than alternative methods. Our code is able to generate values of fluid velocity, pressure, and shear stress at any point within the flow field. As such, it is of value in diagnosing such processing problems as regions of fluid stagnation at which thermal degradation may occur, or regions of excessive shear deformation which lead to thermomechanical damage. It is further able to generate predictions of the forces which must be applied to the melt to achieve the desired flow, and this information is of value in designing processing equipment of optimal efficiency and minimum energy consumption. Ultimately, the project seeks to have developed a versatile and easily implemented analytical tool which may be used routinely by processing engineers, as well as by researchers in rheology seeking solutions to presently intractable problems.

An important secondary goal is the verification of the computer analysis by application to real problems in polymer processing, so that the method may be placed correctly in the context of alternative theoretical approaches which have been used previously.

RESEARCH SUMMARY

Before the inception of the presently funded project, the principal investigator had implemented a basic fluid element, and had performed a series of feasibility computations aimed at demonstrating the applicability of the method to problems in polymer melt extrusion. These included the down-channel and cross-channel velocity and pressure distributions for Newtonian and power-law polymer melts. The results were compared with published closed-form and numerical predictions, and served to illustrate the accuracy and convenience of the finite-element approach. During the first year of the project, this basic code was extended by three research assistants to include the capability for (1) temperature-dependent fluid viscosities, (2) axisymmetric flows, and (3) three-dimensional flows. The incorporation of temperature dependency was restricted initially to uncoupled problems, those for which the temperature field is provided as input data obtained from experimental measurements. The major thrust here was to make available realistic models of temperature-dependent viscosity, and to demonstrate the usefulness of the code in nonisothermal extrusion analysis. Once the experimental temperature distribution was provided, the code was able to generate values of total extruder output and power requirements which agreed with experiment.

The extension of the code to axisymmetric geometries was accomplished by means of a completely rewritten general fluid element, less efficient for simple problems than the two-dimensional element used in the earlier work, but capable of handling a much wider variety of geometry types (two-dimensional, axisymmetric, three-dimensional) and fluid constitutive models. This element was written so as to minimize debugging time and facilitate later modification and extension; as such, it makes extensive use of library routines for matrix operations and is very easy for a new user to understand and modify. The axisymmetric aspect of the element was verified using flows relevant to entry into dies, and to analysis of cylindrical viscometers. The capability of mixed-order elements was also demonstrated in this work. Here, some

element boundaries are interpolated at a higher order than the others; such elements are valuable in refining the grid from coarse to fine as needed for improved accuracy in regions of large velocity gradients.

The three-dimensional capability was incorporated by writing extended shape function and numerical integration routines which were then incorporated into the general fluid element described above. It was not the intention of this project to solve very large problems requiring extensive amounts of computer time and storage such as occur in three-dimensional situations, but it was felt that the capability for such analyses must be present.

Late in the project year, the versatility and easy extendability of the new general fluid element was demonstrated by the ease with which a provision for coupled heat transfer effects could be added. This extension of the code allows for a simultaneous temperature and velocity field computation which makes proper allowance of conduction and viscous heat generation effects, and its output has been found to be in excellent agreement with some model problems for which theoretical solutions are available.

PUBLICATIONS

1. David Roylance, "Use of 'Penalty' Finite Element in Analysis of Polymer Melt Processing," Polymer Engineering and Science, Vol. 20, No. 15, pp. 1029-1034, 1980.
2. In addition, two Master's theses describing the nonisothermal and axisymmetric modeling have been completed in the form of manuscripts, and will be submitted for publication shortly.

ADAPTIVE MATERIALS PROCESSING

PROJECT 1: AUTOMATED MATERIALS PROCESSING: A GENERALIZED VIEW

Principal Investigator: Dr. R. Lund

Personnel: Mr. D. Pinsky

The goal of this project is to define research topics which must be addressed if the use of automation in materials processing is to be advanced. A variety of potential research topics have been suggested during the three Computer Aided Materials Processing Workshops. A set of criteria must be developed to select which topics are appropriate for attention and to set priorities.

To this end, those of us coordinating the workshop sessions propose a tentative conceptual framework for automated processing systems that may be used in classifying the topic areas and in search for additional topics. In exploring for innovative concepts it is essential not only to know what is being sought, but also where to look for it. This framework, then, is suggested as a working tool, and not as a finely tuned model of automation.

Our focus in the workshops has largely concentrated on the physical processes themselves and of the physical support systems (materials handling, inspection, tool, etc.) associated with them. While recognizing the relevance of the information, design and decision systems that surround and interact with the physical processing systems, we have not attempted a full exploration of these areas. To do so would require a study of such areas as scheduling, purchasing, production control, inventory control, quality control, personnel administration, maintenance, tool design, product design and others -- an expansion of scope well beyond the resources of this project. Consequently, the framework is acknowledged to be a circumscribed view of materials processing. It does represent, however, the central functions whose design must precede that of the peripheral support activities.

Our concept of a fully-automated computer aided materials processing system is one which consistently produced useful metal shapes with a minimum of human intervention. It accomplishes this with a high degree of computer-aided integration of functions, in which machine intelligence (computers, microprocessors, vision systems, programmable controllers) is in control of these functions. The system is able to adapt to change in conditions of material, tools, machine capabilities or workplace environment. Finally, the system satisfies societal and economic constraints of practicability.

The physical functions of a CAMP system can be classified under four major headings:

Set-up. Set-up is the preparation of the tools, fixtures, machine conditions, materials, etc. prior to operation of the process. Automation of set-up is particularly important to flexible manufacturing of a variety of products in small lots, where set-up time and costs are a large fraction of total processing time and cost.

Materials Handling. This is the transport, orientation, sorting, mixing, separation, joining of all process solids, liquids, gasses and waste products.

Process Machine Control. This involves controlling the process effectors so that process variables are controlled. These process variables might be thermal, compositional, dynamic (e.g. strain rates), pressure, geometrical, etc.

Inspection. Inspection provides pre-, post-, and in-process diagnostics and feedback of dimensions, metallurgical and compositional properties, position of feedstock, melt, workpieces, finished parts, molds, patterns, and process machinery.

Not only must a CAMP system be able to perform each of these functions automatically, but there should be an integration of these systems into a coherent system, i.e., where there is a direction and automatic relationship between materials handling and set-up, for example, or between materials handling and inspection.

For each of these four processing sub-divisions there will be at least five major components present before automation is possible:

Materials/process models that provide a basic understanding of the behavior of both the materials and the process during actual operating time and conditions. Such models are needed to guide design of the process and as a reference in real-time control of the process.

Control logic, the hardware and software that constitute the decision-making elements of the system. These would include data processing hardware, algorithms, programs and data bases.

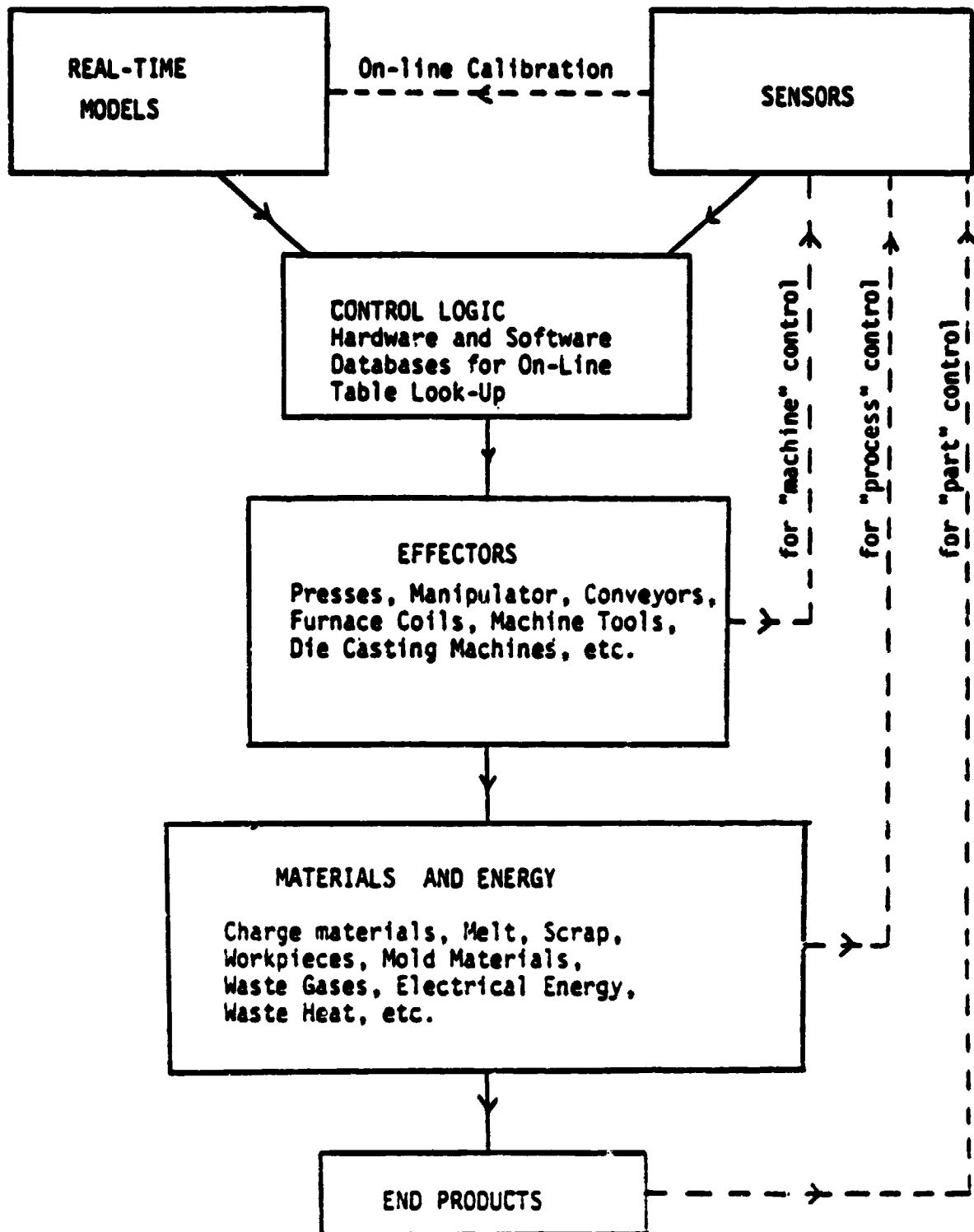
Sensors that measure process behavior and material behavior before, during and after each processing step.

Effectors, the machines that accomplish the physical processing steps, e.g. forging presses, die-casting machines, robot arms, furnaces, conveyors and ladles. Included in this category are the controllers or actuators that are linked to the logic and sensing elements of the system.

Materials and energy that are input to the process and that are processing results. These include feedstock, mold and pattern materials, workpieces, process liquids and solids, electricity, and furnished parts, scrap, waste heat, etc.

Figure 1 illustrates how these component types would interact to perform various tasks. Sensors provide input to the control logic, and calibrate real-time models that also provide input to the control logic. The control logic provides commands to effectors which act upon the materials and energy to produce products. Sensors gather feedback information for each of the three possible feedback loops indicated. Feedback from effectors provides "machine control" or direct control of the process machinery, feedback from materials and energy can provide "process control" or direct control of the process variables, while feedback from end products provides for "part-control" or direct control of the properties of final products.

FIGURE 1
STRUCTURAL SUB-SYSTEM INTERACTION



The importance of accurate materials and processing models, a subject that was repeatedly stressed in the workshops, becomes clear when it can be seen that all other elements of the automated system are dependent upon these models. Each task to be performed must be modeled to determine the optimal configuration and nature of components used. A model of the system is needed to determine how the various tasks should be integrated. The creation of these models requires the use of data bases containing information on component behavior, material and process properties, and perhaps economic, environmental, and social constraints. People with backgrounds cutting across the traditional boundaries of computer science and materials processing are needed to design and test these models properly.

The development of an integrated automated materials processing system could have a structure such as that shown in Figure 2. A planning and design phase culminating in a systems model precedes the development of an actual processing system. The three planning and design inputs are:

Technical Knowledge and Information. This must include all existing knowledge of all possible components, their capabilities, and of process and materials properties. This input is the total of all technical possibilities.

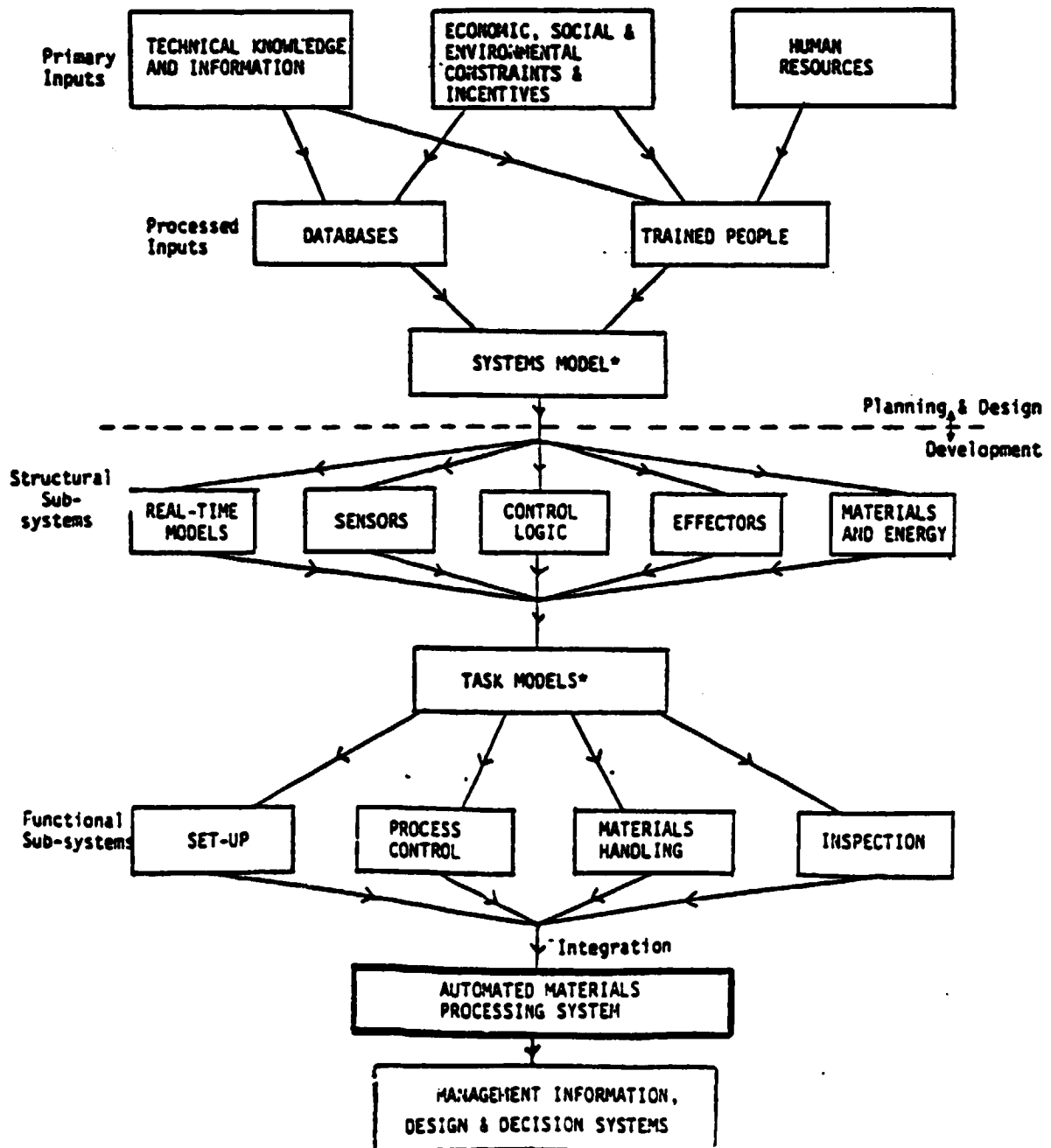
Economic, social and environmental incentives and constraints. This embodies all the motivations for systems development, e.g. financial benefits, elimination of hazardous jobs, reduction in toxic outputs, etc. and the limits placed on such systems by costs, laws, regulations, competition and the like.

Human Resources. The creative human input necessary to synthesize the other primary inputs.

These primary inputs need to be organized before design of a system and its components can be undertaken. People involved must be trained in the appropriate disciplines, understand the reasons for developing automated systems and be aware of the limits within which they can work. These are the trained people in the diagram.

FIGURE 2

FRAMEWORK FOR DEVELOPMENT OF AN INTEGRATED AUTOMATED MATERIALS PROCESSING SYSTEM



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Coding of the available technical information and the constraints imposed into databases provides input for systems models. Parallel input of technical knowledge and constraints will permit cost-benefit analyses of various possible designs of both sub-systems and of complete systems.

Once a system is designed and tested, in modeling or simulation, its system model evolves into task models, and work can move from the planning and design into the development phase. During development, the structural components (real-time models, sensors, control, logic, efforts, materials and energy) are worked out for each of the sub-systems. Integration of these functional sub-systems produces the automated materials processing system. Once the physical system is well-defined, work to tie the system into management information, design and decision systems can proceed. (It is likely that planning and design for user interfaces will have begun earlier in the system development phase.)

The above conceptual framework was used in our study as we approached specific tasks. Topics which appeared, by the third of the three workshops held, to be crucial to the development of automated materials processing include:

- appropriate sensor technology
- modeling of processes
- adaptation of effectors for increased flexibility
- information transfer between dissimilar fields, and
- the development of interdisciplinary expertise

Some recommendations emanating from the three workshops follow in the next section. More detailed reports of the workshops have been presented and distributed; these are referenced at the end of this report^(1,2)

COMPUTER AIDED MATERIALS PROCESSING (CAMP): WORKSHOP RECOMMENDATIONS

1. Information and Technology Transfer

A. Problem: The generation of basic metal processing information and transfer of technology to potential users is inadequate, slow and inefficient.

1. Recommendation: A consortium of universities, industrial firms and non-profit firms and non-profit laboratories is needed to provide the interdisciplinary expertise, information dissemination and pilot-plant capabilities to augment technological innovation in metal processing.

The consortium would serve to bridge the gap now existing between research at the university level and applications engineering in industry.

2. High Temperature Materials Properties

A. Problem: The accuracy of models of metal-forming processes is limited by a lack of physical data.

1. Recommendation: As an initial step, create a task force to locate and disseminate existing data and to generate new data.

Development of new methodologies will constitute a major portion of the task force's work, because existing theories and measurement techniques are largely inadequate.

3. Modeling Applications

A. Problem: The traditional approach to the design of tooling for castings is inadequate for present demands.

Recommendation: Develop affordable stand-alone systems for computer-aided design (CAD) of all steps of casting manufacture.

Potential benefits of this work include the ability to design manufacturing procedures with shorter lead time;

the ability to skip some prototype stages; freedom to assume higher risk in design; reduced energy and materials losses; and a better ability to control the casting process.

- B. Problem: The dependence of the forging industry on skilled operators limits productivity.

1. Recommendation: Develop models that can accurately predict temperature/deformation profiles at various locations in the forging during the forge/heat-treat process.

The benefits include all those under A.1 above, plus that of reducing the industry's dependence on skilled operators by opening the way to open-loop automatic control of forging.

4. Metrology

- A. Problem: Poor communication and technology transfer by sensor manufacturers make it difficult to determine which existing transducers are suitable for application to CAMP.

1. Recommendation: Form a task force within the CAMP program to assess sensor technology needs in metals processing, locate existing technology and identify R&D requirements.

The task force would act both as a clearinghouse for information on sensor needs and availability and as a motivator for research and development in sensor applications to materials processing.

- B. Problem: Present inspection technology for quality evaluation of high-performance metals castings such as turbine blades is expensive and time consuming.

1. Recommendation: Apply a process employing Compton scattering as a means of inspecting castings.

This process is capable of detecting smaller voids than possible by X-ray transmission techniques.

- C. Problem: Metal billets used in forging typically vary by +/- 3% in weight.
1. Recommendation: Develop equipment capable of controlling metal forging input to tighter weight specifications.
- D. Problem: The time lag that currently exists between forging of a part and inspection of the dies and part is too long to allow for a timely process adjustment.
1. Recommendation: Develop inspection systems capable of rapidly detecting variations from the desired weight or dimensions of forged parts.
- E. Problem: Lack of non-destructive techniques for determining the metallurgical and mechanical properties of raw and finished materials has been an obstacle to closed-loop process control.
1. Recommendation: Test existing non-destructive techniques from many fields for their ability to predict the metallurgical and mechanical properties of raw and processed materials.

New LSI and VLSI technologies should enable instrumentation systems to make measurements of process parameters over much shorter successive time intervals.

5. Process Innovation

- A. Problem: Casting processes for small high performance parts such as turbine blades lack reproducibility and control of microstructure.
1. Recommendation: Develop centrifugal casting processes for manufacturing small parts such as turbine blades.

Centrifugal casting of small parts could increase yields and reproducibility for high value cast parts while reducing the cost of casting by about 20 percent.

B. Problem: Ferrous castings have poor mechanical properties.

1. Recommendation: Apply the rheocasting process to ferrous castings.

The possibility of using rheocasting to effect improvements in ferrous castings similar to those accomplished in aluminum castings should be investigated.

C. Problem: Low volume casting requires large investment in tooling and substantial lead time before a part can be produced.

1. Recommendation: Develop single molds (mold families) that are capable of producing more than one casting geometry.

D. Problem: No methods currently exist for controlling the effect of gravity on the microstructure of castings.

1. Recommendation: Investigate the potential of using strong electromagnetic fields to control the microstructure of castings.

E. Problem: Current techniques for casting single- and columnar-grain structures are complicated and inefficient.

1. Recommendation: Develop simpler and faster processes capable of producing complex single- and columnar-grain structures with few defects.

F. Problem: Conventional forging processes tend to consume excessive amounts of energy, materials and labor.

1. Recommendation: Apply near-net shape forging technologies to mass production of parts.

2. Recommendation: Explore techniques to reduce heat consumption during billet heating, transfer and forging.

3. Recommendation: Investigate the application of CAD/CAM techniques for the design and manufacture of forging dies and of preforms, and for control over the forging process.

4. Recommendation: Explore the application of the "Part Controller Paradigm" as an approach to fully automated open-die forging.

G. Problem: Production of aircraft shafts is very expensive due to poor material utilization and expensive I.D. machining.

1. Recommendation: Apply rotary-forging to shaft manufacturing.

H. Problem: Flexible manufacturing systems combining metal-cutting operations have demonstrated the value of integrated computer-managed systems. No such systems exist in metals processing.

1. Recommendation: Develop programmable powder metallurgy, a flexible manufacturing process which uses materials efficiently.

I. Problem: Gravitational effects, atmospheric contamination and the need to contain the process hamper the terrestrial processing of many alloys.

1. Recommendation: Develop zero gravity materials processing techniques that can be used to manufacture materials in space.

6. Robotics

A. Problem: The application of "vision" systems to metals processing has not been adequately investigated.

1. Recommendation: Survey current vision approaches to determine applicability to CAMP.

B. Problem: Commercially available robots are either too slow or too delicate for application to mass production of hot forgings.

1. Recommendation: Develop robots that can increase the productivity of forging while operating within the hostile forging environment.

- C. Problem: There are no useful criteria for selecting manipulation systems for CAMP applications.
 - 1. Recommendation: Establish quantitative criteria for selecting manipulation systems for CAMP applications.
- D. Problem: Finishing of castings is highly labor-intensive.
 - 1. Recommendation: Develop easily programmable, versatile automated systems for removing excess material from castings.
- E. Problem: Goal oriented robots capable of functioning in unstructured environments cannot be developed due to lack of basic technical information.
 - 1. Recommendation: Research the fundamental topics identified in this section that are related to CAMP systems.

REFERENCES

- 1. R. T. Lund and D. A. Pinsky, "Computer-Aided Materials Processing," Center for Policy Alternatives, MIT, Cambridge, Ma., January 1980.
- 2. R. T. Lund and D. A. Pinsky, "Computer-Aided Materials Processing," Center for Policy Alternatives, MIT, Cambridge, MA., May 1980.

IV. MATERIALS PROCESSING RESEARCH, MASSACHUSETTS INSTITUTE
OF TECHNOLOGY

This section summarizes ongoing Materials Processing research at Massachusetts Institute of Technology being conducted in a variety of Departments, Laboratories, and Centers. The research involves a total of 47 faculty members, 40 staff, and 120 graduate students. The Table of Contents at the beginning of this report lists the projects and the page on which the research abstract will be found.

PRIMARY PROCESSING METALS

Faculty: J. P. Clark
J. F. Elliott
M. C. Flemings
T. B. King
T. Ring
D. Sadoway
J. Szekely

Staff: M. Choudhary
G. B. Kenney

SUMMARY

Primary processing research includes work in mineral beneficiation, extraction metallurgy (reduction and refining) and production of primary solid shapes such as ingots and continuously cast slabs and billets. Seven faculty members are involved, but most also have research programs which are described under other classifications. The research deals with assessments of energy and raw material requirements for primary production as well as basic experimental studies of focusses used in extraction and purification of metals. Professor Elliott has continued his studies of the melting of direct reduced iron in electric arc furnaces and has initiated a study of fast fluidized bed reactors. Professors Flemings, Clark, Sadoway, Szekely, and Dr. Kenney have been involved in an assessment of the technology of magnesium production. Professor King has studied the interaction of reactive gases, introduced into a plasma arc, with iron alloys. Professor Sadoway has begun work on electrodeposition of metals from molten slats. Professor Szekely, in addition to his process modelling work, is studying the gas-solid reactions which take place in the iron blast furnace. Professor Ring is starting work on some aspects of separation processes.

Energy Requirements for Melting DRI (Metalized Iron Ore) and Steel Scrap

Fragmented steel scrap and DRI materials are of increasing importance as raw materials for electric arc furnace steelmaking. A study is underway of factors that affect the rate of heating of metal particles that are suspended in a boiling slag. Currently the factors that control the composition and rate of evolution of gases evolved from DRI particles are being studied. This interest arises because the gas-forming reactions may absorb or release heat and the liberation of gas from a particle will influence the motion of the slag near the particle and thereby also influence the transfer of heat from the slag to the particle.

Sponsor: Department of Energy

Faculty: J. F. Elliott

Graduate Student: R. J. O'Malley

Flow of Gases and Solids in a Fast Fluidized Bed Reactor

The fast fluidized bed reactor shows promise of being an important type of reactor in the non-fuels minerals industry. An experimental 8 inch diameter, 30 foot high, stainless steel reactor is now under construction. The first stage in the work is a study of the recirculation of the fine solids and of the flow of gases in the system. The next stage will be a study of the transfer of heat in the system.

Sponsor: Office of Surface Mining, Department of the Interior (Program in the Mining and Minerals Resources Research Institute of M.I.T.)

Faculty: J. F. Elliott

Graduate Students: V. Vejins, C. Ribaudo

Primary Production of Magnesium

Magnesium, with a density less than two thirds that of aluminum, is an important, domestically available, light weight material which offers substantial potential energy savings to the transportation sector. The magnesium program was initiated in 1976 to consider the energy efficiency and economic viability of expanded magnesium production and use in the automotive sector. An international conference was also convened at M.I.T. in 1977 to consider the production and use of magnesium, the most energy efficient automotive material with respect to net life cycle energy use. Work has recently been completed on a technical and economic assessment of current and proposed magnesium primary production technologies as a basis for future programming in process research and development.

Sponsor: Department of Energy

Faculty: J. P. Clark, M. C. Flemings, D. R. Sadoway,
J. Szekely

Staff: G. B. Kenney

Publications:

1. Report from the International Conference on Energy Conservation in the Production and Utilization of Magnesium, edited by Merton C. Flemings, et al., Conference held at MIT, Cambridge, Ma., May 1977.
2. G. B. Kenney and J. P. Clark, "Magnesium: Energy Panacea?", American Metals Market - Minor Metals Section, August 18, 1977.
3. G. B. Kenney and J. P. Clar, "An Analysis of Pricing in the Domestic Magnesium Industry", Proceedings of the Council of Economics of the IME, March 1978.
4. G. B. Kenney, An Analysis of the Energy Efficiency and Economic Viability of Expanded Magnesium Utilization, Garland Publishing Series of "Outstanding Dissertations Bearing on Energy", 1979.
5. M. C. Flemings and G. B. Kenney, "Materials Research for the Fuel Efficient Automobile", Report to the Transportation Systems Center, U.S. Department of Transportation, October 1979.

6. M. C. Flemings and G. B. Kenney, "Materials Substitution and Development for the Light Weight, Energy Efficient Automobile", Report to the Office of Technology Assessment, Congress of the United States, February 1980.
7. G. B. Kenney, D. R. Sadoway and M. C. Flemings, "An Assessment of the Potential for Magnesium Penetration of the U.S. Automotive Industry", Proceedings of the 37th International Magnesium Association.
8. J. P. Clark and G. B. Kenney, "The Dynamics of International Competition in the Automotive Industry. Part I: A Framework for Analyzing the Dynamics of Intermaterial Competition", submitted for publication to Materials and Society, January 1981.
9. G. B. Kenney and J. P. Clark, "The Dynamics of Intermaterial Competition in the Automotive Industry. Part II: A Case Study of the Demand for Magnesium", submitted for publication to Materials and Society, January, 1981.

Kinetics of Interaction of Arc Plasmas with Liquid Metals

When a transferred plasma arc is used to melt metals, the gas used to support the arc is normally argon. Gases such as nitrogen are dissociated in the arc and the atomic species is, generally, much more reactive than the molecular species. It has been shown in this work that, when nitrogen is added to the plasma gas, it dissolves extremely rapidly in liquid iron and the amount of dissolved nitrogen reaches a steady-state solubility well above the value for equilibrium with molecular nitrogen. The steady state solubility increases as the percentage of the nitrogen in the gas increases, up to about 30% N_2 , when a maximum value is reached. The value is also increased markedly by increasing the oxygen content of the iron. A quantitative theory of the solution process has been established. Studies have also been carried out on iron-chromium, iron-nickel, and iron-manganese alloys. When hydrogen is also added to the plasma gas, the rate of nitrogen solution and the value of the steady-state solubility are markedly reduced. Hydrogen

has also been shown to accelerate the rate of desorption of nitrogen.

Work is continuing using hydrogen to deoxidize and decarburize.

Sponsor: National Science Foundation

Faculty: T. B. King

Graduate Student: J. Katz

Transport Phenomena in Improved Electrochemical Cell Design for the Production of Magnesium

Increased use of magnesium as a structural material in transportation vehicles will significantly reduce fuel consumption. At present the restricted use of magnesium by the automotive industry is as much the result of inadequate capacity as price. To learn how transport phenomena in molten salt electrolysis cells affect magnesium production rates the effects of (i) forced convection of the electrolyte (ii) electrode configuration: vertical vs horizontal: monopolar vs bipolar and (iii) applied electromagnetic field will be studied. With the use of transparent laboratory magnesium electrolysis cells, not only will cell operating characteristics be measured, but the electrolysis process itself will be observed visually. The results of this work will serve to guide future developments in high yield cell designs.

Sponsor: Department of Energy

Faculty: D. R. Sadoway

Electrochemical Processing of Deepsea Nodules

In almost all high-temperature electrodeposition processes, the product metal is molten, e.g., aluminum, magnesium,

sodium. This avoids the difficult problem of controlling the morphology of the deposit. Such a solution is not practical for manganese which melts at 1244°C. However, it should be possible to electrowin Mn onto a liquid cathode such as molten zinc with which it forms a low melting alloy. The objective of this study is to determine the conditions under which Mn may be recovered electrochemically from its chloride, as such would relate to an integrated operation to process deepsea nodules. The results would impact upon electrochemically processing onto host cathodes the analogous silicon-based system.

Sponsor: Unsupported

Faculty: D. R. Sadoway

Gas-Solid Reactions

In terms of tonnages handled, the reduction of iron oxides and the gasification of coke in the iron blast furnace are perhaps the two most important metallurgical applications of gas-solid reaction systems.

The work which is being carried out is largely experimental, aimed at developing an improved understanding, how the solid structure and the mode of preparation affects the rate at which coke particles react with CO_2/CO gases under conditions, which are representative of the iron blast furnace.

Parallel with this investigation the rate of iron oxide reduction is also being studied so that a composite picture may be constructed of the coupled reactions that take place in the iron blast furnace.

Work is also in progress to study iron oxide reduction under conditions, which are representative of the direct reduction processes. Here the emphasis is to examine how

the composition of the reactant gas affects the rate of reaction.

Sponsor: Nigerian Government, HYL Corporation (Mexico)
Inland Steel Corporation

Faculty: J. Szekely

Staff: I. Gaballah, N. Towhidi, J. K. Yoon

Graduate Student: J. Berrun

Purification by Fractional Melting (M. C. Flemings)

See "Solidification Processing", p. 135.

Continuous Casting of Steel (M. C. Flemings)

See "Mathematical and Experimental Modeling", p. 104.

Surface Quality of Steel Ingots (M. C. Flemings)

See "Solidification Processing", p. 135.

Deoxidation Reactions During Solidification of Steels
(J. F. Elliott)

See "Solidification Processing", p. 135.

Turbulence Phenomena in Metals Processing (J. Szekely)

See "Mathematical and Physical Modeling of Materials", p. 104.

Electrochemically Driven Flows in Materials Processing
(J. Szekely)

See "Mathematical and Physical Modeling of Materials", p. 104.

Fluid Flow Studies in Electroprocessing (D. R. Sadoway)

See "Mathematical and Physical Modeling of Materials", p. 104.

MATHEMATICAL AND PHYSICAL MODELLING OF MATERIALS
PROCESSING

Faculty: T. W. Eagar
M. C. Flemings
D. K. Roylance
D. Sadoway
J. Szekely

Staff: G. J. Abbaschian
D. Aderibigbe
C. W. Chang
G. Chang
M. Choudhary
T. DebRoy
N. El-Kaddah

SUMMARY

Professor Szekely's major area of research is mathematical and physical modelling of metals processing with major efforts underway on (1) turbulence, (2) electromagnetically driven flow, and (3) gas-solid reactions. Professor Roylance continues his work on numerical modelling of polymer melt processes. Professor Sadoway is modelling electroprocessing and Professor Flemings has modelling studies underway on electroslag casting and continuous casting.

1. MATHEMATICAL AND PHYSICAL MODELLING OF METALS PROCESSING OPERATIONS (J. Szekely)

Turbulence Phenomena in Metals Processing

There are many practical metals processing systems, where molten metal or slag phases undergo turbulent recirculating flow and where the characteristics of this flow play a major role in determining the overall process kinetics. The purpose of the research is to obtain an improved fundamental understanding of the nature of these flows and then to apply this understanding to the solution of practical problems.

This work involves mathematical modelling, viz the solution of the turbulent Navier-Stokes equations, physical model experiments, viz the use of laser anemometry to characterize

the turbulence parameters and the flow fields in water model systems, and plate scale experiments to verify the models. The actual problems currently tackled include the erosion of blast furnace hearths, mixing and desulfurization kinetics in ladle metallurgical operations, AOD steelmaking, hot metal desulfurization and dust removal from gases.

Sponsors: National Science Foundation, primary sponsor; fellowship support from the Brazilian Government, the People's Republic of China and Nippon Steel Corporation

Faculty: J. Szekely

Staff: G. Chang, N. El-Kaddah

Graduate Students: L. Britto, R. Figueira, J. H. Grevet,
K. Shirabe

Electromagnetically Driven Flows in Materials Processing

Electromagnetically driven flows play an important role in many metals processing operations, such as Electro-slag Refining, Electro-slag and Arc Welding, Electric Arc Steel-making, Induction Stirring and the like. The purpose of this program is to develop a quantitative representation of the electromagnetically driven fluid flow phenomena in these systems.

The current work includes the modelling of ESR systems and the concerning pool profiles and temperature profiles. The theoretical predictions have been found to be in excellent agreement with measurements obtained both in the laboratory and on industrial scale installations.

Work is also in progress on the modelling of Electro-slag and Arc Welding operations; the emphasis is to relate the role played by the principal operating parameters in determining the structure and the properties of the welds

produced. Here again, the theoretical predictions were found to be in good agreement with the measurements. The research concerning the modelling of electric arc furnaces is aimed at representing the plasma region formed between the electrodes, with the ultimate objective of defining the optimum arc length for a given set of operating conditions.

Electromagnetically driven flows also play an important role in the work aimed at modelling grain refining in space processing applications. Here the specimens are positioned by electro-magnetic forces, which may also induce motion. The purpose of the work is to define the fluid motion resulting from the positioning forces, both during the flight and in the land based experiments. This understanding of the fluid flow field should be helpful in the development of grain refining modules.

Sponsor: National Science Foundation

Faculty: J. Szekely

Staff: M. Choudhary, J. McKelliget, M. Ushio

Gas-Solid Reactions

In terms of tonnages handled, the reduction of iron oxides and the gasification of coke in the iron blast furnace are perhaps the two most important metallurgical applications gas-solid reaction systems.

The work which is being carried out is largely experimental, aimed at developing an improved understanding, how the solid structure and the mode of preparation affects the rate at which coke particles react with CO_2/CO gases under conditions, which are representative of the iron blast furnace.

Parallel with this investigation the rate of iron oxide reduction is also being studied, so that a composite picture

may be constructed of the coupled reactions that take place in the iron blast furnace.

Work is also in progress to study iron oxide reduction under conditions, which are representative of the direct reduction processes. Here the emphasis is to examine how the composition of the reactant gas affects the rate of reaction.

Sponsor: American Iron and Steel Institute

Faculty: J. Szekely

Staff: J. Berrun, I. Gaballah, N. Towhidi, J. K. Yoon

2. FLUID FLOW STUDIES IN METALS ELECTROPROCESSING
(D. R. Sadoway)

Molten salts are very important solvent systems in which the electrodeposition of a wide variety of metals may be conducted. However, solid electrodeposits from molten salts are typically incoherent, powdery and/or dendritic. To understand better the electrodeposition process, fluid flow patterns in the electrolyte will be observed in order to determine how mass transport affects the morphology of the metal deposit. Studies will be conducted both in aqueous electrolytes in which coherent solid electrodeposits are produced, as well as in transparent molten salt electrolytes. Process variables, such as current density and composition of the electrolyte, will be adjusted to change the morphology of the electrodeposit and, thus, to permit the study of the nature of electrolyte flow in relation to the quality of the electrodeposit. The results of this work will be helpful in electrochemical cell design and will serve as a data base for subsequent mathematical modelling of fluid flow in such systems.

Sponsor: National Aeronautics and Space Administration

Faculty: D. R. Sadoway

Graduate Student: A. Abdelmassih

Undergraduate Student: P. T. Rogers

3. NUMERICAL MODELLING OF POLYMER MELT PROCESSES
(D. K. Roylance)

Finite element techniques are being used to model the velocity, stress, and temperature fields which exist during such polymer melt processing operations as extrusion and injection molding. The computer codes are being developed and tested initially for steady but nonisothermal flows of Newtonian, shear-thinning, and viscoelastic fluids, and will eventually be extended to include transient and free-surface cases. The ability to model these flows in an economic and accurate manner will be of considerable value in optimizing processing operations so as to minimize thermal and mechanical degradation of the polymer, and to develop equipment of improved efficiency.

Sponsor: NSAS, AMMRC, Draper Laboratories

Faculty: D. K. Roylance

Graduate Students: B. Collins, C. Douglas, G. Frecaut, D. Gollo

4. MODELLING SOLIDIFICATION PROCESSES (M. C. Flemings)

Electroslag Casting

This program is a mathematical and experimental model of the electroslag casting process, including study of thermal behavior, macrosegregation, and internal stresses.

Sponsor: National Science Foundation

Faculty: M. C. Flemings

Staff: M. Simpson, Y. Yerebakan

Graduate Student: A. Jain

Continuous Production of Steel

Continuous casting of steel is a commercial reality but major energy savings could be made if steel could be economically cast in thin strips, closer to the dimensions of the final rolled product. This project comprises experimental and mathematical modeling of the manufacture of steel strip, especially by the "Rheocasting" process.

Sponsor: Department of Energy

Faculty: M. C. Flemings

Graduate Student: T. Matsumiya

Heat and Fluid Flow (in Welding) (T. W. Eagar)

See "Welding Research", p. 156.

CERAMICS PROCESSING RESEARCH

Faculty: H. K. Bowen
R. L. Coble
R. M. Cannon
A. Bleir
B. J. Wuensch

Staff: J. H. Haggerty

SUMMARY

A new emphasis on processing of ceramic materials was begun at M.I.T. three years ago with the establishment of the Ceramics Processing Research Laboratory. The recognized purpose of this effort was to develop a processing science base for the ceramics industry. Because of unique institutional problems (at universities, national laboratories and corporations), there has not been a strong base in ceramics processing science as there has been in physical ceramics. Thus, part of the effort at M.I.T. is to form a strong and interactive coalition between M.I.T., the government agencies and the ceramics producer and user industries. Thirteen companies have joined the consortium, over 50 companies have made visits to the campus during the past 15 months to discuss research results, and several companies are making preparations to send their staff members for "internships" in the Laboratory.

The research on processing of ceramics is led by 5 faculty members and 1 senior research scientist and involves 4 research scientists and 4 post-doctoral scientists, 24 graduate students, and 8 undergraduates. Prof. Coble continues his innovative research on experiments and models for sintering and microstructure evolution; Prof. Cannon has developed models and data for understanding the kinetics of grain boundary motion and of pore coarsening; Prof. Wuensch has developed new materials for fuel cells and batteries; Dr. Haggerty has developed new experimental techniques using lasers for forming fine, monosized powders

and for forming stable and metastable structures from liquids, and solar materials research in conjunction with M.I.T. Energy Laboratory; Prof. Bleier joined the faculty this year and has begun unique research on colloidal science and ceramics processing; and Prof. Bowen has developed research programs on the presintering science necessary for controlled green microstructures.

In addition to the facilities in the Center for Materials Science and Engineering, much of this work takes place in the Ceramics Processing Research Laboratory located in Building 12. The laboratory and facilities manager is Dr. Richard L. Pober.

1. LASER PROCESSING (J. S. Haggerty)

A facility, consisting of 3 high power CO₂ lasers and peripheral equipment, has been established to conduct directed energy materials processing research. The equipment is being used to conduct processing research in four distinct areas with non-metallic materials. One custom designed, 1300 watt laser is integrated into a unique crystal growth facility. It is being used to produce high purity, high melting point crystals of oxide, carbides and borides in highly controlled atmospheres. The same apparatus is being used to splat quench various glasses and metastable materials which have been equilibrated in previously inaccessible atmospheres. Another system has been developed to synthesize small diameter, uniform spherical powders of Si, SiC, and Si₃N₄. These powders are used to supply the powder processing research. The third apparatus is being used to investigate a novel laser driven, photo-induced chemical vapor deposition process.

Sponsors: Defense Advanced Research Projects Agency,
Standard Oil of Indiana, MIT Cabot Fund,
National Science Foundation, National
Aeronautics and Space Administration

Faculty: J. S. Haggerty

Staff: W. R. Cannon, S. C. Danforth, J. Flint

Graduate Students: R. Marra, H. Sawhill, L. Schioleter

Undergraduate Students: K. Elcess, M. Gavriel, C. Kerwin,
M. Schmair, B. Sheldon

Publications:

1. W. R. Cannon, S. C. Danforth, J. H. Flint, J. S. Haggerty and R. A. Marra, "Synthesis of Ceramic Powders from Laser Heated Gas Phase Reactants", Proceedings SPIE 23rd Annual International Technical Symposium, San Diego, Calif., August 1979 (in print).
2. J. S. Haggerty, W. R. Cannon, "Sinterable Powders from Laser Driven Reactions", Chapter in Laser Induced Chemical Processes, Ed., J. I. Steinfeld, Plenum Pub. Co., New York, NY (in print).
3. S. C. Danforth, J. H. Flint, W. R. Cannon, J. S. Haggerty, "Laser Synthesis of Silicon Nitride Powders", Laser-Solid Interactions and Laser Processing, AIP Conference Proceedings (in print).
2. PROCESSING OF CERAMIC POWDERS (H. K. Bowen and J. S. Haggerty)

The most critical problem, limiting the extensive use of ceramic materials, is that high technology ceramics cannot be reliably and reproducibly manufactured. The focus of our research program is on the physics and chemistry of controlled particulate formation (size, size distribution, dispersion, phase and chemical composition, and shape) and of controlled packing of particles (no particle density gradients). The ceramic systems being studied are: Al_2O_3 , BaTiO_3 , $\text{BaFe}_6\text{O}_{19}$, ZnO , Si , SiC , Si_3N_4 , SiO_2 , TiO_2 and TiB_2 . Powders are made by homogeneous gas phase nucleation (laser driven) or by controlled growth in aqueous and non-aqueous solutions. The colloidal dispersion parameters are being studied and models and techniques developed for controlled coagulation of the powders into shapes which are subsequently densified. Low firing temperatures and

shorter sintering times are necessary in addition to better control of the microstructure and thus the physical properties.

The technological goals of this research are directed towards the use of ceramics as multilayer Si-chip carrier, capacitors, turbine and diesel engine components, permanent magnets, and varistors.

Sponsors: AVX, Corning, Solid State Dielectrics, Union Carbide, Vitramon, Ford, GM-Delco, Hitachi, Tektronix, IBM, Exxon, Department of Energy

Faculty: A. Bleier, H. Kent Bowen and J. S. Haggerty

Staff: R. L. Pober, J. Blendell, S. Mizuta

Graduate Students: E. Barringer, C. Huynh, M. Parish, M. Strauss, M. Green, R. Riman, N. Jubb, D. Swanson, E. Tormey, R. Garcia

Undergraduate Students: L. Robinson, N. Levoy

Theses:

1. P. G. Lemaire, "Pore Migration in KCl Due to a Temperature Gradient", B.S., June 1980.
2. L. Robinson, "The Adsorption of Menhaden Fish Oil and Glycerol Trioleate on Sr-La-Ferrite from Toluene", Ph.D., June 1980.

Publications:

1. E. S. Tormey, et al., "Adsorption of Dispersants from Nonaqueous Solutions", to be published in Proc. of Conf. on Surfaces and Interfaces in Ceramics and Ceramic-Metal Systems, July 1980, Berkeley, CA.
2. H. K. Bowen, "Processing BaTiO₃ Capacitors: Dispersion of Powders", M.I.T. Ceramics Processing Research Laboratory Report #5, September 1980.
3. H. K. Bowen, et al., "Basic Research Needs on High Temperature Ceramics", Materials Science and Engineering, Vol. 44, 1980, pp. 1-56.

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3. MATERIALS FOR SOLAR ENERGY (J. S. Haggerty, D. Adler, S. C. Danforth)

Materials processing research is being conducted in two solar energy areas. In the first, graded index of refraction anti-reflection (AR) coatings are being developed on silicate glass by preferentially removing one phase of a phase separated glass. When used on covers of flat plate collectors, these broad band AR coatings increase the extractable heat by 30 - 50%. The second area involves several materials processing programs for photovoltaic devices. Our analyses indicate that amorphous processes offer the best chance of achieving required cost objectives. Consequently, we have limited our research to this focus. Processes to improve carrier life times in chalcogenide glass semiconductors have been investigated to take advantage of their low cost and adjustable band gap. Processes to control the nucleation and growth processes in amorphous silicon are being studied to make use of the low cost amorphous deposition processes and the high efficiency of crystalline Si. The laser CVD deposition process is being developed because of low manufacturing cost and superior properties through better process control.

Sponsors: Department of Energy, SERI, MIT Cabot Fund, 3M

Faculty: J. S. Haggerty, D. Adler

Staff: S. C. Danforth, I. Kohatsu, T. Gattuso, J. B. Vander Sande, D. Imeson

Graduate Students: A. Iqbal, M. Meunier, F. Van Gieson

Undergraduate Students: S. Barros, B. Cinnamon, J. Devaud, J. Hillman, C. Kerwin, B. King, B. Sheldon

Theses:

1. A. Iqbal, "Determination of Surface Chemistry of Graded-Index, Antireflective Films on Glass", S.M., January 1981.
2. T. Moyer, "Effects of Alkalies on the Electrical Properties of Amorphous Se-Te Thin Films", S.M., September 1980.

3. D. Millar, "Investigating the Transition from Consumable to Renewable Resources with Dynamic Net Energy Analysis", B.S., June 1979.
4. B. Cinnamon, "Analysis of an Open Film Solar Collector", B.S. Thesis, June 1980.
5. T. Kramer, "Nitriding of Silicon Formed by Laser Decomposition by Silane", S.B., June 1980.

Publications:

1. S. C. Danforth, J. S. Haggerty, D. Imeson, A. Iqbal, and J. B. Vander Sande, "Microstructural Analysis of Broad-Band Antireflective Films on Glass", presented at American Ceramic Society Annual Meeting, April 1980, in print J. Am. Ceram. Soc.
2. S. C. Danforth, J. S. Haggerty, F. Van Gieson and I. Kohatsu, "Laser Induced Controlled Nucleation and Growth Process for Large Grained Polycrystalline Silicon", presented at Materials Research Society Annual Meeting, November 1980, in print as symposium proceedings.

4. SINTERING AND MICROSTRUCTURE EVOLUTION (R. L. Coble, R. M. Cannon)

Most of the important technological developments for processing ceramic materials have resulted from theoretical models of sintering and grain growth coupled with an enormous number of experimental measurements. The efforts at M.I.T. over the past 25 years have been at the forefront of the development of these concepts, and most recently has succeeded in modelling the very complex simultaneous processes which occur during the firing of ceramic greenware.

Because of the extreme sensitivity of ceramic materials to impurities and additives, and because of the difficulties in characterizing fine powders, these theoretical analyses provide guidance to the selection of experimental parameters (T, P, composition, particle size and distribution) for a critical set of measurements to test the basic theories as well as providing guidance to the ceramic processors. These analyses are also demonstrating the importance of the local

distribution of porosity, impurities or dopants, and grain or particle size in determining the densification process and microstructure evolution.

Numerous model materials have been chosen which have widely varying difference in diffusion coefficients, vapor pressures, surface and grain boundary energies, etc. These include: Al_2O_3 , ZrO_2 , Au, ZnO, Si, SiC, MgO, LiF, $\text{ThO}_2\text{-ZrO}_2$. In each case, fundamental studies are performed which relate the basic thermochemical forces and transport coefficients to the observed evolution of the sintered microstructure.

Some of the particularly exciting recent accomplishments are:

1. establishing the conditions for sintering covalently bounded materials such as silicon, including the effects of vapor and surface transport on coarsening, and of boron additives on surface chemistry and transport;
2. development of infrared window materials ($\text{ThO}_2\text{-ZrO}_2$) with improved fracture toughness;
3. demonstration of the effects of trace impurities and dopants on the mobility of grain boundaries in hot forged LiF;
4. analyses of the potential contribution of diffusion induced grain boundary migration (DIGM) in ceramic materials; and
5. the development of new techniques using slips to avoid agglomerates and inhomogeneous porosity as the case with usual processing operations.

Sponsors: Department of Energy, National Science Foundation, Defense of Advanced Research Projects Agency

Faculty: R. L. Coble, R. M. Cannon

Graduate Students: J. Dynys, T. Kuo-wen, W. Hong, C. Handwerker, R. French, W. Coblenz, T. Ketchum, A. Glaeser, C. Gasdaska, T. Coyle, R. Fuentes, M. O'Connor

Undergraduate Students: A. Roshko, A. Kobrin, R. Marinos

Theses:

1. T. Gattuso, "Slow Defect Diffusion in KCl", Ph.D., September 1980.
2. A. Kobrin, "Sintering SiC", B.S., June 1980.

Publications:

1. J. M. Dynys, R. L. Coble, W. S. Coblenz, and R. M. Cannon, "Mechanisms of Atom Transport during Initial Stage Sintering of Al_2O_3 ", Sintering Processes, Ed., G. C. Kuczynski, Plenum Publ. Corp., 1980, pp. 391-404.
2. A. Glaeser, H. K. Bowen and R. M. Cannon, "Grain Boundary Migration in LiF", to be published in Proc. of Conf. on Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems, July 1980, Berkeley, CA.
3. W. S. Coblenz, J. M. Dynys, R. M. Cannon, and R. L. Coble, "Initial Stage Solid State Sintering Models. A Critical Analysis and Assessment", Sintering Processes, Ed., G. C. Kuczynski, Plenum Publ. Corp., 1980, pp. 141-157.
4. M. F. Yan, R. M. Cannon and H. K. Bowen, "Effect of Grain Size Distribution on Sintered Density", submitted to J. Am. Ceram. Soc.

5. SYNTHESIS AND PROPERTIES OF FAST-ION CONDUCTORS
(B. J. Wuensch and I. Kohatsu)

Fast-ion conductors, materials which display ionic electrical conductivities up to six or eight orders of magnitude larger than normal ionic compounds (i.e, up to 5 reciprocal ohm-cm), find important application in fuel cells and battery systems. We are conducting a broad study of such materials, which includes synthesis and power processing of potential new conductors, fabrication of sintered specimens for measurement of electrical properties, growth of single crystals, and precise neutron and x-ray diffraction measurements to provide insight into the mechanisms of the fast-ion conduction process. The materials which are currently the subject of exploratory

synthesis and processing are alkali metal conductors of relevance to battery systems. Potential new conductors include several alkali metal silicates and titanates, and nitrogen-based ceramics. In addition, novel solid-solution series are being prepared with systems which have previously been demonstrated to display fast-ion conduction. Among these are NASICON ($\text{Na}_3\text{Zr}_2\text{SiPO}_{12}$) and LISICON ($\text{Li}_{3.5}\text{Zn}_{0.25}\text{GeO}_4$) related systems. Phases for which single crystals have been synthesized and for which diffraction studies have begun are primarily the prototype cation-disordered Ag and Cu conductors. These are ideal systems for critical examination of models for the distribution and thermal motion of the mobile cations as they constitute a large fraction of the scattering density in these materials. These phases include Cu_2S , CuAgS , Ag_3SI and Ag_2Se .

A variety of processing techniques are employed, depending upon the system of interest. Solid state reaction of component oxides or salts are frequently employed, as are hydrothermal reaction and preparation of gels. The growth of single-crystal materials employs (again depending on the system) hydrothermal techniques, flux growth or vapor transport.

Sponsors: Department of Energy, Lawrence Berkeley Laboratory

Faculty: B. J. Wuensch

Staff: I. Kohatsu, A.-K. Ekholm

Graduate Students: C. L. Skarda

Publications:

1. R. J. Cava, F. Reidinger and B. J. Wuensch, "Conductivity Mechanisms in the Superionic Phases of AgI and Ag_2S as Determined by Neutron Diffraction", in Fast Ion Transport in Solids: Electrodes and Electrolytes, P. Vashishta, J. N. Mundy and G. K. Shenoy, Eds. Elsevier North Holland, 1979, pp. 217-220.

2. R. J. Cava, F. Reidinger and B. J. Wuensch, "Single-Crystal Neutron Diffraction Study of the Fast-Ion Conductor -Ag₂S Between 186 and 325°C, J. Solid State Chem., Vol. 31, 1980, pp. 69-80.

EFFECT OF PROCESSING ON POLYMER/COMPOSITE STRUCTURE AND PROPERTIES

Faculty: F. J. McGarry
R. M. Rose
D. K. Roylance
C. S. P. Sung
G. E. Wnek

Staff: J. F. Mandell

SUMMARY

After many decades of regarding polymer processing as a series of unrelated, often empirical, disciplines dealing with the formation and shaping of materials, the industry has come to realize that further advances in the vitality and economic health of the field will require a more consistent and rational point of view in which processing is viewed as a participant in the underlying triad of relationships which comprise materials science and engineering. This triad includes processing as it influences material structure, and ultimately properties. Although several MIT faculty are presently involved in research dealing with various aspects of what might be termed polymer processing, a group of faculty has formed under the auspices of the Department of Materials Science and Engineering whose work is centered specifically around the theme of processing-structure-properties, and this group has developed enough coherence to justify its inclusion in this report under a common heading. Their work spans the full range of subdisciplines of polymer science and engineering: Prof. Wnek is concerned primarily with polymer chemistry and synthesis, Prof. Sung treats structure modification and optimization through processing as the unifying theme of her research, Prof. Roylance has been developing methods of melt flow modeling as an important aspect of his work in processing structure-property relations of polymers, Prof. McGarry's longstanding interest in mechanical properties of composites has always included

processing as an important aspect, and Prof. Rose has extended his expertise in biomedical materials research to include polymer processing effects. Although any classification of the diverse research interests of this group is of course somewhat arbitrary, they are in fact unified by a common interest in processing and its role in shaping structure, and the following descriptions are intended to summarize their principal goals and approaches.

1. POLYMER SYNTHESIS (G. E. Wnek)

Electrically Conducting Polymers

Polyacetylene has recently been shown to attain high conductivity (ca. $10^3 \Omega^{-1} \text{ cm}^{-1}$) upon chemical doping with electron donors or acceptors. Potential applications of these conductive derivatives are limited by the intractability and oxidative instability of polyacetylene. Three approaches are being explored in order to enhance the processibility and reduce the instability of this material. First, copolymers of acetylene and various monomers are being synthesized with the aim of reducing strong inter-chain interactions while still maintaining reasonably high conductivity upon doping. Recent work concerning acetylene-methyl-acetylene copolymers has shown that the copolymer films are reversibly swellable in common organic solvents. Studies of copolymers processing larger pendant groups (ethyl, propyl, etc.) are in progress. The second approach involves the preparation of blends of polyacetylene and various materials such as polyethylene and polystyrene. The primary goal is to utilize the second component of the blend as a protective coating for inhibition of oxidation of polyacetylene. Current work focuses on polymerization of acetylene within a polyethylene matrix which has been impregnated with an appropriate catalyst.

In addition, the polyethylene-polyacetylene films will be stretched to various extension ratios and examined by polarized uv-vis spectroscopy to provide information concerning polarized electronic transitions in polyacetylene. Finally, post-polymerization reactions are being investigated. Of particular interest is the interaction of polyacetylene with protonic acids. Recent experiments in our laboratory indicate that polyacetylene films are extensively swelled in the presence of certain protonic acids and may even be partially solubilized.

Sponsor: Seed Funding, Department of Materials Science and Engineering, MIT

Faculty: G. E. Wnek

Graduate Student: M. E. Galvin

Publications:

1. G. E. Wnek, J. C. W. Chien, F. E. Karasz, M. A. Druy, A. G. MacDiarmid, Y. W. Park, and A. J. Heeger, "Variable Density Conducting Polymers: Conductivity and Thermopower Studies of a New Form of Polyacetylene, $(CH)_x$ ", J. Polym. Sci., Polym. Lett. Ed., Vol. 17, 1979, p. 779.
2. G. E. Wnek, J. Capistran, J. C. W. Chien, L. C. Dickinson, R. Gable, R. Gooding, K. Gourley, F. E. Karasz, C. P. Lillya and K.-D. Yao, "Studies in Conducting Polymers", Symp. on Electrical Properties of Polymers, ACS Meeting (Las Vegas, August 1980), in press.
3. J. C. W. Chien, G. E. Wnek, J. Hirsch, F. E. Karasz, A. G. MacDiarmid and A. J. Heeger, "Electrically Conductive Acetylene-Methylacetylene Co-Polymers - Synthesis and Properties", Macromolecules (submitted for publication).

2. PROCESSING-STRUCTURE RELATIONS IN POLYMERS (C. S. P. Sung)

Effect of Injection Molding

The injection molding process is likely to introduce non-homogeneous structure and orientation on the polymer surface as compared to its core, due to the rapid cooling effect from the mold surface. As a sensitive way of measuring surface orientation, we have developed a modified attenuated total internal reflection IR dichroism technique by using a symmetrical double-edged internal reflection crystal. The molecular orientation as measured by this technique was indeed greater on the surface than in the core of the injection molded polypropylene plate, a tendency confirmed by birefringence. This non-destructive technique is more surface-sensitive than birefringence measurement.

Sponsor: Office of Naval Research

Faculty: C. S. P. Sung

Graduate Students: J. P. Hobbs, M. K. Tse

Publications:

1. M. K. Tse and C. S. P. Sung, "Comparison of Crystallinity and Molecular Orientation between Surface and Bulk of Some Polymers", ACS Org. Coatings and Plastics Chem., Vol. 42-1, 1980, p. 734.
2. C. S. P. Sung, "A Modified Technique for Measurement of Orientation from Polymer Surfaces by Attenuated Total Reflection IR Dichroism", submitted to Macromolecules.

Structure of RIM Processed Polyurethane

Reaction injection molding is becoming an important process for making large automotive parts. Due to the requirement of easily pumpable monomers, liquid diisocyanate which

contains a cyclic adduct in addition to pure MDI is preferred. We are studying the effects of the cyclic adduct on the final structure and properties of lightly cross-linked polyurethanes. In some cases, even after post-curing and aging, we observe a significant extent of residual reactivity due to the cyclic adduct. We are also studying the effect of a primary diol versus a secondary diol used as a chain extender.

Sponsor: Rogers Corporation

Faculty: C. S. P. Sung

Graduate Students: J. P. Hobbs, C. Oehl

Structure/Properties of Interface in Al_2O_3 /Polyethylene Composite

In composites such as an Al_2O_3 /polymer joint, adhesion of the interfaces is important, especially in terms of environmental durability. We are interested in understanding the role of so-called coupling agents utilized to improve adhesion. We are using sapphire, single crystalline aluminum oxide, as a model surface because of its experimental advantages. The characterization of the adsorbed coupling agents and two interfaces is carried out by FT-IR, ESCA and SEM. Attempts are made to correlate the structure of interfaces to the joint strength such as peel strength.

Sponsor: Air Force Office of Scientific Research,
Army Research Office

Faculty: C. S. P. Sung

Graduate Students: I. J. Chin, A. Kaul, S. Ni (Tufts U.),
N. H. Sung

Publications:

1. N. H. Sung, S. Ni and C. S. P. Sung, "IR Studies of Organic Silanes and Titanates Adsorbed on Single Crystalline Aluminum Oxide and E-glass Fibers", ACS Org. Coatings and Plastics Chem., Vol. 42-1, 1980, p. 743.

2. N. H. Sung and C. S. P. Sung, "Structure of the Silane Coupling Agents Adsorbed on Single Crystalline Aluminum Oxide as Studied by FT-IR and ESCA", 35th Annual Technical Conference, Reinforced/Plastics/Composites Institute, SPI, Section 23-B, New Orleans, 1980.
 3. N. H. Sung, A. Kaul, S. Ni, C. S. P. Sung and I. J. Chin, "Role of Organo Silanes and Organo Titanates in Promotion of Adhesion Strength of Aluminum Oxide-Polyethylene Joint", 36th Annual Technical Conference, Reinforced Plastics/Composites Institute, SPI, in press, Washington, 1981.
3. PROCESSING OF THERMOPLASTICS (F. J. McGarry, D. K. Roylance, R. M. Rose)

Cold Forming of Polyvinyl Chloride

Polyvinyl chloride, one of the largest volume plastics, is especially sensitive to heat so melt forming operations require close controls to avoid thermal degradation of the polymer. The situation is exacerbated with formulations intended for higher temperature applications, therefore great benefit would derive from forming methods which could be carried out economically at or near room temperature. The purpose of this research is to identify and explore such methods suitable both for powder and sheet PVC. Considerable success has now been achieved in powder forming of homogeneous PVC samples with promising mechanical properties.

Sponsor: B. F. Goodrich Company

Faculty: F. J. McGarry

Staff: J. F. Mandell

Graduate Students: J. H. Chen, M. C. Kenney

Rapid Solidification of Thermoplastics

The free volume content in glassy thermoplastics depends upon the rate of cooling through the glass transition

temperature. It strongly affects certain macroscopic mechanical properties via the process known as aging. Very rapid cooling and solidification of metals has produced amorphous structures with unusual properties. The purpose of the present research is to look for similar effects in glassy polymers containing abnormally large free volume. Some exploratory work with crystalline polymers may be done also. Careful measurements on quenched thin films of polyvinylchloride and polystyrene do show a significant increase in free volume as compared with control specimens.

Sponsor: National Aeronautics and Space Administration

Faculty: F. J. McGarry

Staff: J. F. Mandell

Graduate Students: A. Agrawal, H. Lee

Numerical Modeling of Polymer Melt Processing

Finite element techniques are being developed to model the velocity, stress, and temperature fields which exist during such polymer melt processing operations as extrusion and injection molding. Computer codes have been developed and verified for steady nonisothermal flows of Newtonian, shear-thinning, and viscoelastic fluids in which the effects of viscous heat generation and heat transfer are incorporated. Research is presently ongoing aimed at extending the models to include transient and free-surface effects. The ability to model these flows in an economic and accurate manner will be of considerable value in optimizing processing operations so as to minimize thermal and mechanical degradation of the polymer, and to develop equipment of improved efficiency.

Sponsors: National Aeronautics and Space Administration,
Army Materials and Mechanics Research Center,
Draper Laboratories

Faculty: D. K. Roylance

Graduate Students: B. Collins, C. Douglas, G. Frecaut,
D. Gollob

Publication:

1. D. K. Roylance, "Use of 'Penalty' Finite Elements in Analysis of Polymer Melt Processing", Polymer Engineering and Science, Vol. 20, 1980, p. 1029.

Processing of Ultrahigh Molecular Weight Polyethylene

The performance of ultrahigh molecular weight polyethylene of total joint replacements depends crucially on how the reacted polymer is processed into the solid implant component, as processing determines the ultimate molecular weight and defect distribution.

Evaluation of performance depends on accurate total joint simulations and assessments of wear and mechanical and chemical breakdown, and comparisons with clinical retrievals. This is done in several ways with the polymer processing as the independent variable.

Sponsor: NIH

Faculty: R. M. Rose, A. M. Crugnola (University of Lowell)

Staff: G. Arndt, E. Goldfarb, I. M. Puffer, M. Ries

Graduate Student: W. R. Cimino

Undergraduate Students: A. Casavant, N. Goldberg

Theses:

1. W. R. Cimino, "The Comparative Wear Evaluation of Polyethylene for Total Joint Arthroplasty", S.M., June 1980.
2. W. D. Ries, "Wear Behavior of Polyethylene Components Used in Total Joint Prostheses", S.M., June 1979.

Publications:

1. R. M. Rose, A. M. Crugnola, W. R. Cimino, and M. D. Ries, "The In-Vivo Performance of Polyethylene Components of Total Joint Replacements", Proceedings of Implant Retrieval Conference at the National Bureau of Standards, May 1-2, 1980.
2. R. M. Rose, H. J. Nusbaum, H. Schneider, M. Ries, I. Paul, A. Crugnola, S. R. Simon and E. L. Radin, "On the True Wear Rate of Ultrahigh Molecular Weight Polyethylene in the Total Hip Prosthesis", J. of Bone and Joint Surg., Vol. 62-A, No. 4, June 1980, pp. 537-549.
3. R. M. Rose, A. Crugnola, M. Ries, W. Cimino, I. Paul, and E. L. Radin, "On the Origins of High In Vivo Wear Rates in Polyethylene Components of Total Joint Prostheses", Clinical Orthopaedics and Related Research, 1979, pp. 277-296.
4. R. M. Rose, H. J. Nusbaum, I. Paul, A. Crugnola, and E. L. Radin, "Wear Mechanisms for Ultrahigh Molecular Weight Polyethylene in the Total Hip Prosthesis", J. of Appl. Polymer Sci., Vol. 23, 1979, pp. 777-789.

Exploratory Research in Nondestructive Testing

This project is aimed at exploring the properties of defects in polymers and polymer-matrix composites as dielectric singularities and at identifying convenient methods of detecting defects in Ti weldments, based on similar approaches.

Sponsor: Office of Naval Research

Faculty: R. M. Rose

Staff: I. M. Puffer

Undergraduate: J. Parse

4. PROCESSING OF THERMOSETS (F. J. McGarry)

Modification of Anhydride Cured Epoxy Resins

Anhydride cured epoxy resins often are used in electrical potting or encapsulating applications. Resistance to elevated temperatures, thermal shock and good dielectric properties are essential. This work involves liquid rubber additions to improve thermal shock resistance without sacrificing heat resistance or dielectric properties. To achieve such, it is necessary that a two phase structure be formed, with the elastomer in discrete particles. If the elastomer forms a solid solution with the epoxy, serious losses of heat resistance are encountered.

Sponsor: Siemens, A.G.

Faculty: F. J. McGarry

Graduate Student: A. Hussain

Publication:

1. A. Hussain and F. J. McGarry, "Toughening of Anhydride Cured Epoxy Resins", M.I.T. Department of Materials Science and Engineering Research Report R80-2, March 1980.

ELECTRONIC MATERIALS RESEARCH

Faculty: H. C. Gatos
T. B. King
W. M. Rohsenow
A. F. Witt
J. Lagowski (Senior
Research Associate)

Staff: P. Becla
L. Huang
K. Isozumi
S. Isozumi
M. Kaminska
Y. Nanishi
X. F. Yang
E. Bourret
T. Carlberg
R. Crouch
Z. Xing
Q.-M. Zhou

SUMMARY

The research activities of the group are focused on semiconductor materials and aimed at the establishment of quantitative relationships underlying Crystal Growth Parameters - Materials Properties - Electronic Characteristics - Device Applications. The overall program evolves about the following main thrust areas: (1) Crystal Growth - novel approaches to engineering of semiconductor materials; (2) Investigation of materials properties and electronic characteristics on a macro- and microscale; (3) Surface properties and surface interactions with the bulk and ambients; (4) Electronic properties controlling device applications and device performance.

The group has traditionally focused on the establishment of a scientific basis for melt and solution growth of semiconductor systems with special emphasis on macro- and microsegregation. Related research clarified the nature and origin of rotational and non-rotational dopant striations and resulted in the development of current induced growth interface demarcation and electro-epitaxy which are now generally adopted procedures in processing research and technology. Efforts to improve composition control in doped semiconductor crystals led to the first application of heat

pipes and transverse magnetic fields to Czochralski-type growth system and constitute the basis for a major research commitment to the exploration of the potential of reduced gravity environment.

Recent developments in solid state device technology exposed the need for improvements in electronic materials processing and particularly for more stringent composition control. To improve our ability to interact with and to be responsive to the changing needs of industry, we have refocused the primary research activities to include systems of general concern involving Si, GaAs, InP, HgCdTe and PbSnTe and are preparing to engage in growth studies of CdTe. With support of DARPA, NASA, Airforce and industry, we have been able to establish the capability of large diameter silicon crystal growth and processing which will in the near future permit the preparation and characterization of wafers to be used for subsequent device research. In collaboration with the National Magnet Laboratory, a silicon growth facility is currently under construction which will operate under computer control and permit the application of vertical and horizontal magnetic fields.

To permit an expansion of the scale of research activities, MIT has recently provided 6,000 sq. ft. of new laboratory space which is expected to become operative this summer.

1. DEEP-LEVEL FREE MELT-GROWN GaAs

High quality electron trap-free GaAs crystals were grown for the first time from the melt in a horizontal Bridgman-type apparatus. Such crystals were obtained by determining experimentally an optimum As vapor pressure which was maintained constant by a sodium heat pipe and by introducing minute amounts of Ga_2O_3 in the melt. At the optimum As

pressure, corresponding to 617°C in our system, not only were the electron traps eliminated (as determined by DLTS), but the dislocation density decreased below 100/cm², the compensation ratio reached a minimum, and the minority carrier diffusion length reached the theoretical value of 5 μm. The implications of this "epitaxial quality" bulk GaAs material to device applications is being pursued.

Sponsor: National Aeronautics and Space Administration

Faculty: H. C. Gatos, J. Lagowski

Staff: Y. Nanishi (visiting)

Graduate Student: J. Parsey

Publication: J. Parsey, Y. Nanishi, J. Lagowski and H. C. Gatos, "Deep-Level Free Melt-Grown GaAs", submitted for publication.

2. FORMATION OF RECOMBINATION CENTERS IN EPITAXIAL GaAs DUE TO RAPID CHANGES OF THE GROWTH VELOCITY

It was established that recombination centers in epitaxial GaAs are formed upon abrupt acceleration of the growth. The corresponding effect of abrupt deceleration of the growth is only minor. In the case of backmelting, recombination centers are also introduced, however, not due to backmelting itself, but rather due to the subsequent acceleration of the growth. The abrupt changes in growth velocity were achieved by corresponding changes in the current density during electroepitaxial growth.

Sponsors: National Aeronautics and Space Administration,
National Science Foundation

Faculty: H. C. Gatos, J. Lagowski

Staff: L. Jastrzebski

Publication: L. Jastrzebski, J. Lagowski and H. C. Gatos, "Formation of Recombination Centers in Epitaxial GaAs Due to Rapid Changes in Growth Velocity", accepted for publication.

3. GROWTH OF HgCdTe

Electroepitaxial growth of HgCdTe was initiated, and it was demonstrated that it can be achieved either from Hg-rich or Te-rich solutions. The unavailability of low resistivity CdTe substrate, however, presents a basic problem associated with excessive Joule heating during growth. For this reason an apparatus was constructed for the "isothermal growth" (vapor transport) of thick low resistivity HgCdTe to be used as substitutes for electroepitaxial growth. Layers of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ were obtained with x varying from 0.15 to 0.3. These layers are not only suitable to be used as substrates (low resistivity) but exhibit electron mobilities of the order of $500,000 \text{ cm}^2/\text{V-sec}$, i.e., about one order of magnitude greater than those reported in the literature.

Sponsor: Defense Advanced Research Projects Agency

Faculty: H. C. Gatos, J. Lagowski

Staff: P. Becla (visiting)

Graduate Student: H. Ruda

Publication: P. Becla, J. Lagowski, H. C. Gatos and H. Ruda, "A Modified Approach to Isothermal Growth of Ultra-High Quality HgCdTe for IR Applications", accepted for publication.

4. CATHODOLUMINESCENCE OF InP

Cathodoluminescence studies were carried out on p-type InP having carrier concentrations ranging from 7.2×10^{16} to $7.4 \times 10^{18} \text{ cm}^{-3}$ in the temperature range of 80 to 580°K. It was found that low temperature spectra exhibited peaks at 1.41 and 1.38 eV. These peaks were attributed to band-to-band and band-acceptor transitions, respectively. The dependence of the band-to-band peak on temperature was used to extend knowledge of the temperature dependence of the energy gap of InP to 550°K. It was shown that the half width of the

cathodoluminescence peak can be used for the determination of carrier concentration and carrier concentration inhomogeneities in the material. The variations of the cathodoluminescence peak height with temperature indicated the possibility of Auger recombination for high carrier concentrations ($7.4 \times 10^{18} \text{ cm}^{-3}$) at temperature above 450°K.

Sponsor: National Aeronautics and Space Administration

Faculty: H. C. Gatos, J. Lagowski

Staff: K. Isozumi

Graduate Student: J. Vaughan

Publication: C. H. Gatos, J. J. Vaughan, J. Lagowski and
H. C. Gatos, "Cathodoluminescence in InP",
submitted for publication.

5. GaAs-OXIDE INTERFACE STATES, A GIGANTIC PHOTOIONIZATION EFFECT AND ITS IMPLICATION TO THE ORIGIN OF THESE STATES

Photoionization discharge of GaAs-oxide interfaces led to the identification of discrete states at 0.7 and 0.85 eV below the conduction band. Furthermore, a gigantic photoionization process was discovered leading to the discharge of the 0.7 eV states with rates up to three orders of magnitude greater than those of photoionization transitions to the conduction band. It exhibits a peak 45 meV below the bandgap with a shape similar to acceptor-donor transitions and is attributed to an Auger-like ejection of electrons from deep surface states through energy transfer from photo-excited donor-acceptor pairs. Utilizing this new process, it was shown, for the first time, that both deep levels and shallow donor and acceptor levels can be assigned to Ga and As vacancies.

Sponsor: National Science Foundation

Faculty: H. C. Gatos, J. Lagowski

Staff: W. Walukiewicz

Graduate Student: T. Kazior

Publication: J. Lagowski, W. Walukiewicz, T. Kazior, H. C. Gatos and J. Siejka, "GaAs-Oxide Interface States, A Gigantic Photoionization Effect and Its Implications to the Origin of These States", submitted for publication.

6. GROWTH AND SEGREGATION CONTROL DURING LARGE DIAMETER SILICON CRYSTAL GROWTH

Through DARPA funding and industrial donations, three crystal growth facilities have been acquired capable of silicon crystal growth with diameters ranging from 2.5" to 4" diameters. Those facilities are currently being modified to operate under computer control and to permit the application of horizontal and vertical magnetic fields up to 5 kG during growth. Instrumentation for crystal processing to wafers has been acquired and is being installed. In related work, a model has been developed for the dynamic oxygen concentration in silicon melts. The model is found to be in good agreement with experimental results and to account for first order effects of both the absolute oxygen concentration and its axial variations in grown crystals. Approaches aimed at achieving controllable and axially uniform oxygen concentration in crystals have been suggested. A theory which accounts for the radial segregation of oxygen and carbon in silicon is currently being established.

Sponsor: Defense Advanced Research Projects Agency

Faculty: A. F. Witt

Staff: T. Carlberg

Graduate Students: D. Bliss, H. Herring

Publications:

1. T. Carlberg, T. B. King and A. F. Witt, "Dynamic Oxygen Equilibrium in Silicon Melts During Crystal Growth by the Czochralski Method", accepted for publication in the J. Electrochem. Soc.

2. T. Carlberg and A. F. Witt, "Radial Oxygen Segregation During Czochralski Growth of Silicon", in preparation.

7. HEAT FLOW CONTROL AND SEGREGATION IN DIRECTIONAL SOLIDIFICATION

This research program focuses on the relationship between heat flow and growth and segregation behavior in solidification systems with the thrust being directed toward achieving optimized growth and segregation in directional freezing geometry through controlled heat transfer. Making use of growth interface demarcation and spreading resistance measurements the performance characteristics and basic limitations of conventional Bridgman configurations are determined. The data obtained are used as input for two-dimensional heat transfer calculations and for thermal modelling to establish a basis for the design of a growth configuration which is characterized by one-dimensional heat flow about the crystal-melt interface. A system currently under construction is based on aligned heat pipes for the generation of isothermal regions, separated by an insulated heat-guiding gradient zone. A computer-based control and data acquisition system (which was designed and constructed) is used to optimize temperature stability, and to control in a pre-programmed mode axial and radial thermal gradients in the growth zone. A specially configured data acquisition system provides for complete thermal characterization of the growth facility. The facility includes the capability of growth interface demarcation and thus permits the precise determination of growth rates, the shape of the solidification isotherm and its dependence on controllable systems parameters; it will also allow the exact determination of the location of this isotherm and its relocation under the influence of growth and changing thermal boundary conditions. The thrust of this activity is directed toward the optimization of semiconductor crystal growth in

Bridgman-type configurations. It is believed that this technique, if properly executed, has the potential of yielding materials of a significantly higher degree of perfection than presently obtainable. The technique is moreover ideally suited for studies aimed at improving the theoretical framework for crystal growth and segregation.

This research activity is interactive with the Department of Mechanical Engineering (Prof. W. Rohsenow) and the Department of Chemical Engineering (Prof. R. Brown).

Sponsor: National Aeronautics and Space Administration

Faculty: A. F. Witt, W. Rohsenow

Graduate Students: C. Wang, T. Jasinski, B. Ahern

Publication: C. Wang, J. R. Carruthers, A. F. Witt,
"Transient Crystal Growth and Segregation Behavior
in Vertical Bridgman Configuration", in
preparation.

8. MELT GROWTH OF III-V COMPOUND SEMICONDUCTORS

The growth of compound semiconductor single crystals in which one or more of the constituents exhibit a significant vapor pressure at processing temperatures continues to be a major technological problem. Such materials generally exhibit stoichiometric deficiencies as well as directly or indirectly related crystalline defects. The primary approach to growth, the liquid encapsulated Czochralski method, has been empirically developed and the effects of encapsulants on the melt behavior and the solidification process have so far not been subject of a comprehensive investigation. This research activity is directed toward the optimization of liquid encapsulated Czochralski growth. The characterization of liquid encapsulated melt systems in growth configurations is currently being carried out on model systems at low pressures (GaSb, Ge) but will be extended to high pressure

systems (InP, GaAs, GaP) as relevant characterization data become available. In our ongoing activities the primary focus is placed on the exploration of thermal effects of encapsulants, on heat flow control and related convective melt behavior and on segregation and crystal defect formation. In this context we are also investigating the potential of total melt encapsulation which is expected to lead to increased stoichiometry control and reduced melt contamination. Efforts are also made to develop a means for stoichiometry control after synthesis and encapsulation.

Sponsor: Rome Air Development Center

Faculty: A. F. Witt

Staff: Q.-M. Zhou, R. Crouch, E. Bourret

Graduate Students: E. Pope. M. Wargo

Publications:

1. E. D. Bourret, J. J. Favier and A. F. Witt, "Theoretical Analysis of Directional Melting", submitted for publication.
2. Q.-M. Zhou and A. F. Witt, "Effects of Liquid Encapsulation on Crystal Growth and Segregation During Czochralski Pulling", submitted for publication.

SOLIDIFICATION PROCESSING

Faculty: T. W. Eagar
M. C. Flemings
J. F. Elliott
D. K. Roylance
D. R. Sadoway
J. Szekely

Staff: G. Abbaschian
M. Simpson
Y. Shiohara

SUMMARY

The Solidification Processing activities underway include the studies of Professor Flemings on behavior of semi-solid metals, purification and strengthening by fractional melting; continuous casting; and control of ingot surface quality. Professor Elliott continues his work on formation and growth of inclusions. These studies are summarized below.

In addition there are ongoing studies by many faculty members on rapid solidification. There are studies on crystal growth being conducted by Professors Witt and Gatos. In addition there are studies on experimental and mathematical modeling of solidification processes. These studies are summarized in separate parts of Section IV of this report.

Deformation Behavior of Semi-Solid Metals

This ongoing program is concerned with the fundamental rheological behavior of semi-solid metals. Past work has been on non-dendritic "rheocast metals"; current work is primarily on dendritic solids and on metal powders which are liquid phase sintered under pressure. Engineering applications are to better understand liquid phase sintering phenomena, and to develop improved forming materials and purification methods for materials which are partly liquid.

Sponsor: Army Research Office, Department of Energy

Faculty: M. C. Flemings

Staff: V. Laxmanan
P. Charreyron
M. Suery
A. Lux

Graduate Students: T. Matsumiya, D. Pinsky

Publications:

1. V. Laxmanan and M. C. Flemings, "Deformation of Semi-Solid Sn-15 Pct Pb Alloy", Met. Trans., Vol. 11A, No. 12, December 1980, pp. 1927-1937.
2. T. Matsumiya and M. C. Flemings, "Modeling of Continuous Strip Production by Rheocasting", accepted Met. Trans.
3. A. Lux and M. C. Flemings, "Refining by Fractional Solidification", Met. Trans., Vol. 10B, March 1979, pp. 71-79.
4. A. L. Lux and M. C. Flemings, "Refining by Fractional Melting", Met. Trans. B, Vol. 10B, March 1979, pp. 79-84.
5. M. Suery and M. C. Flemings, "Deformation Behavior of Semi-Solid Alloys", to be published.

Strengthening of Metals by Fractional Melting

Ultra-high strength aluminum alloys are produced by partially melting alloy ingots and "squeezing" out interdendritic residual liquid, thereby drastically lowering impurity levels, and residual second phases. Properties in wrought material produced by these ingots are equivalent to, or better than, the best properties obtained in ingots produced by other means, including consolidation of rapidly solidified powders. Work currently is on 7000 series aluminum alloys. Mechanical properties obtained are in excess of 90,000 psi yield strength, 100,000 psi tensile strength and 10% elongation.

Sponsor: Army Materials and Mechanics Research Center

Faculty: M. C. Flemings

Staff: C.-H. Yeh

Graduate Students: F. Goodwin, T. Piness, M. Gungor

Publications:

1. F. E. Goodwin, P. Davami, M. C. Flemings, "Strengthening of Wrought Aluminum Alloys by Fractional Melting", accepted Met. Trans. A, Vol. 11A, Nov. 1980, pp. 1777-87.
2. P. Davami, F. E. Goodwin and M. C. Flemings, "Strengthening of Cast Aluminum Alloys by Fractional Melting", to be published.

Surface Quality of Steel Ingots

This is an experimental modeling study of factors affecting ingot surface quality in steel ingots and continuous castings. Work to date has been on low melting point alloys, in molds which have one transparent face. High speed photography has been used to record wave motion and meniscus behavior during filling and relate this to surface and subsurface structures obtained. Wave motion and metal-mold heat transfer coefficients have an important effect. Dampening effect on convection of a steady D.C. magnetic field alters the wave motion significantly.

Sponsor: American Iron and Steel Institute

Faculty: M. C. Flemings

Graduate Students: M. Zueletta, D. Stemple

Publications:

1. M. N. Zulueta and M. C. Flemings, "The Development of Surface Features in Ingot Castings", to be published.

Deoxidation Reactions During Solidification of Steels

The formation, growth and agglomeration of secondary deoxidation products during cooling and solidification of steel ingots and castings is being studied. Currently the emphasis is on complex deoxidation products containing manganese, silicon and iron. The relationships among

composition variables, solidification parameters and morphology of the deoxidation products are being studied.

Sponsor: American Iron and Steel Institute

Faculty: J. F. Elliott

Graduate Student: D.-C. Hu

Electromagnetically Driven Flow in Materials Processing
(J. Szekely)

See "Mathematical and Physical Modelling of Materials", p. 104.

Fluid Flow Studies in Metals Electroprocessing
(D. R. Sadoway)

See "Mathematical and Physical Modelling of Materials", p. 104.

Numerical Modeling of Polymer Melt Process (D. K. Roylance)

See "Mathematical and Physical Modelling of Materials", p. 104.

Electroslag Casting (M. C. Flemings)

See "Mathematical and Physical Modelling of Materials", p. 104.

Continuous Production of Steel

See "Mathematical and Physical Modelling of Materials", p. 104.

Rapid Solidification

Nine faculty, nine staff and graduate students, are working on a wide variety of different aspects of rapid solidification. These are detailed in the following section on "Rapid Solidification Processing", p. 139.

Heat and Fluid Flow (in Welding) (T. W. Eagar)

See "Welding Research", p. 156.

RAPID SOLIDIFICATION PROCESSING

Faculty: M. Cohen
M. C. Flemings
N. J. Grant
R. Latanision
R. Kaplow
F. J. McGarry
J. Szekely
J. B. Vander Sande
G. Yurek

Staff: L. Arnberg
P. Domalavage
B. Franetovic
Y. Geffen
J. Megusar
R. Mandell
G. Olson
Y. Shiohara
R. Zrilic

SUMMARY

Rapid solidification comprises a major thrust area of Materials faculty at MIT. Work is proceeding on crystalline and non-crystalline metals, and on polymers. Work is planned on ceramics. Research ranges include fundamental studies on solidification mechanism and resulting structure, innovative processing techniques, properties and applications.

Professor Grant and co-workers continue his broad program focussed on alloys which offer high strength at elevated temperatures, and on the processing methods necessary to achieve these goals. Professor Cohen and co-workers are concentrating on structure and structure-property relations in ferrous alloys. Professor Vander Sande, interacting with most other faculty working in this area, continues his work on structure. Professor Latanision is working on corrosion related aspects and Professor Yurek is studying the high-temperature oxidation resistance of fine-grained alloys. Professor Flemings and co-workers are concentrating on relation of solidification theory to structures produced, and on innovative processes for rapid solidification. Professor McGarry has initiated studies on rapid solidification of polymeric materials. Some current research activities are given below.

1. RAPID SOLIDIFICATION TECHNOLOGY FOR STRUCTURES AND
PROPERTY CONTROL OF HIGH TEMPERATURE METALS
(N. J. Grant)

A rather broad range of programs constitutes the activities of this group. Emphasis remains focused on alloys which offer high strength at elevated temperatures and the processing methods necessary to achieve such goals. The application and study of rapid solidification (RS) to produce new classes of alloys and to achieve superior structures and properties is broadly applied to both microcrystalline and glassy alloys.

Numerous microcrystalline alloy systems have been studied to date, including Al, Cu, Fe, stainless steels, Ni-base superalloys and Co-base superalloys. Glassy alloys are based on transition metal-transition metal combinations and on transition metal-nonmetal alloys. Phenomena of interest include strength, plasticity, toughness, corrosion resistance, superplasticity, fatigue improvements, first wall fusion reactor applications, etc., etc.

Brief paragraphs follow which attempt to attach a flavor to the specific programs underway.

Glass Formation, Alloying Effects on the Glass Transition
and Crystallization Temperature of Ni-Nb Alloys

Effects on deformation processes and fracture as a function of temperature, strain rate, alloying, etc.

Glass Formation, Alloying Effects on the Glass Transition
and Crystallization Temperature of $Pb_{80}Si_{20}$

Deformation studies as a function of temperature and strain rate in the compression mode. Role of alloying on high temperature strength and viscous flow. Crystallization kinetics and the role of crystal content on mechanical behavior.

Production and Study of Superfine Crystalline Alloys
Produced by Conversion of Selected Glassy Alloys

The attainment of grain sizes as fine as 100 to 500 Å is demonstrated from prior glassy (homogeneous) alloys. Resultant grain sizes are very uniform. The aim is to produce ductile, tough, strong alloys which may also have other attractive characteristics such as corrosion resistance, for example.

The Structure and Properties of R.S. Lithium Modified
2024 Aluminum Alloys

Lithium contents up to 3 percent are readily possible in R.S. atomized alloys and result in fine grained (2 to 3 microns), high specific strength, high specific modulus alloys. Studies include measurements of tensile properties, fatigue behavior, fracture toughness.

The Structure and Properties of R.S. 2618 Aluminum Alloy

This alloy, one of the best high temperature ingot alloys, is being studied as R.S. atomized and hot consolidated material, and again after R.S. atomization plus attrition grinding to fine flakes to produce an oxide dispersed 2618 product, which is expected to have significantly improved strength properties from 150 to 250°C.

The Structure and Properties of R.S. X2020

The X2020 type of alloy (Al-Cu-Mn-Li) is recognized as having particularly attractive properties, such as a high specific modulus and high specific strength. This continuing study attempts to optimize such properties while maintaining or improving such other features as notched toughness, notched fatigue behavior, etc. Particular emphasis is being placed on a study of the notched fracture

characteristics in terms of composition, structure, purity, etc.

The Structure and Properties of R.S. Al-Mg-Li Alloys

Whereas the Al-Mg-Li alloys have not shown comparable strength values to those of R.S. X2020 (Al-Cu-Li), the potential for major gains in specific strength and modulus favor the low specific gravity Al-Mg-Li alloys. Detailed studies of structure-property relationships are underway.

The Structure and Property Relationships in X7091, 7075 with Zr + Ni and Other Alloys

Maximum strength values are synonymous with the 7XXX alloys. Major additions of transition metals have been shown to be effective in R.S. 7XXX alloys by changing the chemistry of the phases formed and their size and distribution. In particular, additions of Fe, Ni, Ti, Zr, Mn, Co in various combinations and amounts have had beneficial effects especially on strength, with evidence that toughness and fatigue performance can be maintained at high levels. A number of these alloying combinations are being studied.

High Strength, High Temperature, High Conductivity Copper-Base Alloys

Three distinct areas are being investigated:

- A. M2C Type Alloys (Cu-Mg-Zr-Cr). These alloys with excellent strength at 20°C and excellent strength at 400°C in creep rupture are being examined as conventional ingot product, R.S. atomized powders, and R.S. atomized and attrition milled flakes. The latter two conditions represent oxide dispersed alloys at two oxide contents. Thermal conductivity values are near 80 percent of those of pure copper.

- B. Cu-Ni-Ti Alloys. These alloys in ingot form are stronger than the MZC alloy, but have only about 60 percent of the conductivity of pure Cu; they are also a bit weaker in creep at 400°C. As R.S. alloys, both in powder form and as fine attrited flakes, they have exhibited unusually attractive strength and ductility at 20°C and outstanding creep-rupture properties at 400°C. Studies of thermomechanically processed structures are continuing in a search for further improvements.
- C. The Solution Treating, Ageing and Over-Ageing Behavior of MZC and Cu-Ni-Ti Alloys Produced by Rapid Solidification. These copper alloys undergo complex ageing behavior patterns. The MZC alloy, with precipitates of both Cu_3Zr and Cr, presents additional structural complication when ZrO_2 and Cr_2O_3 are also formed during powder and flake processing. The Cu-Ni-Ti alloys, which harden unusually during quenching from the solution temperature, are further complicated when prepared from R.S. powders and attrited flake material which produce TiO_2 . The presence of the oxide serves to retain the energy of cold work which can obscure some of the benefits of the ageing process. The contributions of both strengthening methods will be determined.

The Development of Cu-10Ni and Cu-30Ni Base Alloys by Tertiary and Quarternary Alloying Additions

These alloys, produced by rapid solidification (ultrasonic gas atomization), will be examined to establish the role of alloying elements such as Fe, Cr, Ti, Mn and others on strength, toughness, salt water corrosion, etc. A number of the alloying elements enhance salt water corrosion as long as they do not form coarse excess phases. The R.S. approach will be used to enhance the control of structure.

The Structure and Properties of O.D.-Type 316 SS Prepared from R.S. Atomized Powders

The production of very fine (minus 50 μm) R.S. powders permits rapid attrition milling down to near micron thick flakes, allowing selected elements in solution in the stainless steel to surface oxidize (Al_2O_3 , BeO , ThO_2 , Y_2O_3) to provide an O.D. alloy for high temperature service. This is an approach to determine whether fine oxide dispersions can be produced by this process to permit cheaper, easier, more reproducible O.D. alloys.

The Structure and Properties of Highly Alloyed Nickel-Base Superalloys Prepared from R.S. Atomized Powders

As with the item above, the aim here is to determine if superfine R.S. powders can be suitably attrited to near micron-thick flakes to provide, for example, 1 to 2 vol pct of Al_2O_3 in a complex alloy such as IN-100. The application, broadly, of O.D. type alloys is restricted by extreme costs and the inability to readily reproduce the best reported properties of such alloys made by more conventional processing methods.

The Superplastic Behavior of Duplex Ferrite-Austenite Stainless Steels

This study has as its aims the determination of the optimum content of ferrite to austenite on superplastic deformation, on strength of the final product, on corrosion resistance and other properties. The role of composition is equally important since the various ratios of ferrite to austenite can be achieved by many alloying combinations. The limited solubility of the ferrite for carbon and nitrogen will permit precipitation of carbides and nitrides in the ferrite. The R.S. process guarantees a fine grain size (3 to 20 μm) in the extruded product.

The Initiation and Growth of Intercrystalline Cracks in γ - γ' Nickel-Base Superalloys, in γ -Carbide Cobalt-base Superalloys, and in γ -Oxide Nickel-Base Oxide Dispersed Alloys

Following such definition, samples will be prepared for fatigue testing as pre-cracked specimens to determine the further growth of cracks under a wide range of conditions of temperature, cycle frequency, hold times, etc. The aim is to determine whether one of these three basic alloy systems is better suited for further alloy development for service from 650 to 1200°C.

First Wall Fusion Reactor Materials Prepared by R.S. Technology

The extreme demands on materials to operate as first wall materials with high dpa, helium generation and precipitation, radiation creep, etc., calls for unusually stable, strong alloys. R.S. techniques can produce fine grained, homogeneous alloys with selected second phase precipitates or dispersions uniformly distributed in the matrix, and of controlled particle size and shape. Extensive alloying, far beyond that possible through ingot technology, has already been demonstrated. Selected experimental alloys suitable for fission reactor exposure to simulate a fusion reactor is another important issue. Using R.S. technology, a range of type 316 stainless steels with increasing TiC content have been prepared and are in test; type 316 SS with a fine dispersion of Al_2O_3 is being prepared; ferritic Fe-BeO alloys, and selected copper-base alloys, have also been prepared and are undergoing neutron irradiation and heavy ion irradiation.

Sponsors: National Science Foundation (via the M.R.L. program at MIT), Department of Energy (several divisions), Army Research Office, International Copper Research Association, National Aeronautics and Space Administration, U.S. Navy (David W. Taylor, Naval Ship and Research Center), AMAX Fellowship, Michelin Fellowship.

Faculty: N. J. Grant

Staff: L. Arnberg
P. Domalavage
B. Franetovic
Y. Geffen
J. Megusar

Publications:

1. V. Anand, A. J. Kaufman, and N. J. Grant, "Rapid Solidification of a Modified 7075 Aluminum Alloy by Ultrasonic Gas Atomization", Proceedings of Second International Conference on Rapid Solidification, March 1980, Eds. R. Mehrabian, B. H. Kear, M. Cohen, Claitor's Pub. Div., Baton Rouge, LA.
2. B. C. Giessen, N. J. Grant, D. P. Parker, R. C. Manuszewski, and R. M. Waterstrat, "The Niobium (Columbian)-Palladium Constitution Diagram", Met. Trans., Vol. 11A, 1980, p. 709.
3. N. J. Grant, "The Potential for Increased Use of Manganese in the Metal Industry", Deepsea Mining, October 1979, Ed. J. T. Kildow, M.I.T. Press, Cambridge, MA, pp. 140-147.
4. N. J. Grant, S. Kang, and W. Wang, "Structure and Properties of Rapidly Solidified 2000 Series Al-Li Alloys", First International Conference on Al-Li Alloys, Georgia Tech, 1980 (in print).
5. J. Megusar, A. S. Argon and N. J. Grant, "Plastic Flow and Fracture in $Pd_{80}Si_{20}$ near T_g ", Materials Science and Engineering, Vol. 38, 1979, pp. 63-72.
6. J. Megusar, L. Arnberg, J. Vander Sande, and N. J. Grant, "Optimization of Structure and Properties of Path A Prime Candidate Alloy (PCA) By Rapid Solidification", submitted for publication to Journal of Nuclear Engineering.
7. J. Megusar and N. J. Grant, "Stabilization and Strengthening of $Pd_{80}Si_{20}$ Metallic Glass", submitted for publication to Journal Materials Science and Engineering.
8. K. K. Sandaran and N. J. Grant, "Structure and Properties of Splat Quenched 2024-Aluminum Alloy Containing Lithium Additions", Materials Science and Engineering, Vol. 77, No. 2, July 1980, p. 213.
9. V. K. Sarin and N. J. Grant, "The Effect of Thermo-mechanical Treatments on P/M Cu-Zr and Cu-Zr-Cr Alloys", Powder Metallurgy International, Vol. 11, No. 4, November 1979, p. 153.

2. RAPID SOLIDIFICATION PROCESSING OF IRON-BASE ALLOYS (J. B. Vander Sande, M. Cohen, R. Kaplow)

The Office of Naval Research (ONR) has been supporting a research effort to determine the relationships between metallurgical structure and properties in rapid solidification processed iron-base alloys. This research program involves three faculty, one senior staff member, and four students.

The research work being undertaken in this program can be divided into four parts: microstructural characterization of rapidly solidified (RS) steels, grain growth retardation in RS steels, fracture toughness of RS steels, and decomposition of Fe-base amorphous alloys. Each of these areas is briefly described below.

Microstructural Characterization of Rapidly Solidified Steels

In an effort to obtain a qualitative assessment of the fundamental solidification variables associated with solidification at rapid solidification rates, two austenitic steels have been observed in the form of powders and after consolidation. The two steels, a high-sulfur, 303 stainless type and a high-phosphorus steel (Fe-Cr-Ni-P) have been prepared by the centrifugal atomization technique pioneered by Pratt and Whitney Aircraft, West Palm Beach, Florida.

Scanning transmission electron microscopy (STEM) has been used for microstructural and microchemical analysis of these two rapidly solidified steels. In the high sulfur, 303 stainless steel extremely small sulfide particles (MnS) have been observed at the cell walls and in the intracellular region of the solidification structure of individual rapidly solidified powder particles. Moreover, composition profiles have been obtained by the STEM across

cell walls in these powders which indicate that a high degree of chemical homogeneity has been obtained. This microstructural and microchemical analysis has provided a format for describing the microstructural evolution that occurs as a function of increasing cooling rate for this alloy. At the fastest cooling rates, segregationless solidification has been observed; as the cooling rate is decreased, a non-regular cell structure develops and at the slowest cooling rates available ($\sim 10^4$ °C/sec), a regular cell structure is observed. A similar study has been initiated on the Fe-Cr-Ni-P steel. In the individual powder particles observed in this steel a regular cell structure is observed and is delineated by the presence of a Cr- and P-rich amorphous phase which is a continuous phase and surrounds the cell interiors.

For the high-sulfur, 303 stainless a comparison has been made of the microstructures of powders, consolidated powder product, and conventionally processed material with two important findings. First, the sulfide particles are found to be two or three orders of magnitude smaller in size, and more uniformly distributed in the consolidated product when compared to the conventionally processed material. Second, the general microstructure of the powders are retained in the consolidated powder product.

Grain Growth in Rapidly Solidified Steels

Rapidly solidified steels have been found to exhibit an unusual resistance to grain coarsening at high temperatures. Comparison of conventionally processed and rapidly solidified 9Ni-4Co and 2Mo steels revealed that the rapidly solidified material retains a grain size of ~ 20 μm at 1200°C, where conventionally processed material coarsens to several hundred microns. Thus far the only possible boundary pinning mechanism suggested by transmission and

scanning transmission electron microscopy analysis is a fine dispersion of inclusions, principally MnS. It is not yet clear, however, whether these particles are present in sufficient quantity to account for the observed coarsening resistance. Detailed examination of the coarsening behavior of extruded rapidly solidified material indicated preferential boundary pinning at prior powder particle interfaces, probably due to free surface segregation during powder particle solidification. More recent observations on hot pressed material with spherical powder particle "domains" showed that, although there is some preferential pinning at these interfaces, the same high temperature coarsening resistance prevails in the particle domain interiors, regardless of the domain shape. Hence the coarsening resistance is a result of rapid solidification and not powder processing, as such.

Fracture Toughness of Rapidly Solidified Steels

The use of high austenitizing temperatures is known to increase the sharp crack toughness (K_{IC}) of some steels, attributed primarily to dissolution of void initiating particles; simultaneously, the blunt notch toughness (C_V) and ductility are found to decrease due to excessive grain coarsening. The high temperature grain coarsening resistance of the rapidly solidified steels described above may allow improvement of K_{IC} without loss of C_V energy and ductility. Preliminary toughness measurements on a 9Ni-4 Co-0.6C steel indicate that the K_{IC} of rapidly solidified material is equal to or superior to that of conventionally processed material (after high austenitizing treatment). Future efforts will focus on 4340, 300M, and HP310 steels where the benefits of high austenitizing treatments are well established. Both K_{IC} and Charpy C_V energy will be studied as a function of austenitizing treatment.

Decomposition of Fe-Base Amorphous Alloys

The prospects for using the glassy phase of materials as the starting point for achieving (by thermomechanical treatment) technically advantageous phases and phase-morphologies which cannot be attained otherwise have provided the motivation for this work. Research has been focused on Fe-based alloys, especially Fe-B alloys, which are of intrinsic interest in the glassy state because of their unique magnetic properties.

A variety of Fe-B binary alloy samples, covering a wide range of composition, have been investigated. Experimental information has been obtained using X-ray diffraction, Mossbauer spectroscopy, differential scanning calorimetry (D.S.C.), transmission electron microscopy, and electron diffraction.

The constant-heating-rate D.S.C. measurements often show a small, post-crystallization exothermal "bump", possibly due to a change in the form of the Fe_3B precipitation. Isothermal D.S.C. measurements have been made on a series of alloys to determine the kinetic properties of the transformations. Transmission electron microscopy (almost entirely on $\text{Fe}_{81}\text{B}_{19}$ alloys) shows that in-situ thermal studies of thinned specimens do not fully reflect the behavior of "bulk" samples. As-quenched, nominally 100% glass samples sometimes contain large, isolated Fe_3B particles. During TEM in-situ annealing, α -iron forms earliest in the thinnest regions, while Fe_3B tends to form in the thicker regions, in areas where the matrix is still partially amorphous. The Fe_3B particles show contrast patterns indicative of internal strain and diffraction patterns indicative of fine structure within each particle. In contrast to these observations, bulk-treated samples (thinned post-treatment), exhibit Fe_3B only where the local

matrix is entirely amorphous, and that Fe_3B is always tetragonal and shows no diffraction evidence for internal fine structure. In addition, the Fe_3B morphology is quite different for bulk and pre-thinned samples. Other special studies under way include high precision density measurements (to clarify the situation regarding the relative positions of the boron atoms) and Mossbauer measurements of high-boron content samples predominantly in the α -phase, to clarify the issues of extreme boron concentrations in the metastably formed phase and the electronic/magnetic interactions between the boron and iron atoms.

Sponsor: Office of Naval Research, AMAX Foundation,
Bethlehem Steel

Faculty: J. B. Vander Sande, M. Cohen, R. Kaplow, and
G. B. Olson

Staff: H. C. Ling

Graduate Students: M. Suga, J. L. Goss, T. Kelly, K. S.
Tan, P. Fleyshman, C. Y. Hsu, J. Montgomery,
K. Taylor

Undergraduate Students: D. Cocke, B. Leibowitz,
L. Janavicius

Theses:

1. M. Suga, "Austenitic Grain Growth in Rapidly Solidified 9Ni-4Co Steels", S.M., August 1980.
2. J. L. Goss, "Austenitic Grain Growth and Precipitation Strengthening in Rapidly-Solidified Alloys", S.M., September 1980.

Publications:

1. M. Cohen, B. H. Kear, and R. Mehrabian, "Rapid Solidification Processing - An Outlook", Proceedings on Rapid Solidification Processing - Principles and Technologies, Claitor's Publishing Division, Baton Rouge, LA, 1980, p. 1.
2. K.-S. Tan, T. Wahl, and R. Kaplow, "Monitoring Metastable Phases and Grain Structures Derived from Glassy Alloys", Proceedings on Rapid Solidification Processing - Principles and Technologies, Claitor's Publishing Division, Baton Rouge, LA, 1980, p. 112.

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3. M. Suga, J. L. Goss, G. B. Olson, and J. B. Vander Sande, "Austenitic Grain Growth Characteristics in Rapidly Solidified Martensitic Steels", Proceedings on Rapid Solidification Processing - Principles and Technologies", Claiborne's Publishing Division, Baton Rouge, LA, 1980, p. 364.
 4. T. F. Kelly and J. B. Vander Sande, "A STEM Analysis of Two Rapidly Solidified Stainless Steels", Proceedings on Rapid Solidification Processing - Principles and Technologies, Claiborne's Publishing Division, Baton Rouge, LA, 1980, p. 100.
 5. S. S. Hansen, J. B. Vander Sande, and M. Cohen, "Niobium Carbonitride Precipitation and Austenite Recrystallization in Hot-Rolled Microalloyed Steel", Met. Trans., Vol. 11A, March 1980, p. 387.

3. SOLIDIFICATION BEHAVIOR AT RAPID RATES
(M. C. Flemings, J. Vander Sande)

These programs are on (1) development and application of solidification theory to rapid solidification and solidification at high undercoolings, (2) experimental studies on structures obtained by rapid solidification, and relation to theory, and (3) development of innovative processes for producing rapidly solidified materials.

The research is sponsored by National Aeronautics and Space Administration, National Science Foundation, and Army Materials and Mechanics Research Center.

Rapid Solidification of Binary Alloys

Simple binary alloys are being rapidly solidified by splat cooling, ribbon quenching, and laser or electron beam surface melting. Cooling rates and interface growth velocities are calculated and structures produced related to solidification theory. As example, the amount of residual second phase is measured in rapidly solidified aluminum-copper alloys, using the SEM and quantitative metallography; also by using X-ray methods. Composition profiles

in other binary alloys are measured using STEM. Results are compared to the developing theories of solidification of rapidly solidified alloys.

Sponsor: National Science Foundation

Faculty: M. C. Flemings, J. Vander Sande

Staff: G. Abbaschian

Graduate Students: H. Cairnie, M. L. Putman, L. Masur

Theses:

1. M. L. Putman, "Second Phase Measurements in Rapidly Solidified Aluminum-Copper", S.M., February 1981.
2. H. S. Cairnie, "Quantitative Determination of Non-equilibrium θ Phase in Rapidly Solidified Al-Cu", S.M., December 1980.

Publication:

1. G. J. Abbaschian and M. C. Flemings, "Effect of Supercooling and Inoculant on the Structure of Levitated Fe-Ni Alloy", to be published.

Rapid Solidification of Magnesium Alloys

An exploratory study of structures obtainable in commercial and binary magnesium alloys by splat cooling, ribbon quenching, and laser glazing has begun with emphasis on the relation to solidification theory.

Sponsor: Army Materials and Mechanics Research Center

Faculty: M. C. Flemings

Graduate Student: J. T. Burke

Undercooling and Rapid Solidification

One part of this study comprises dispersion of droplets of molten metal alloys in fluxes and slag to obtain large degrees of undercooling following the methods of Turnbull and Perepezko. Methods are being studied of combining the

large undercoolings obtained with rapid solidification. Structures are examined by electron microscopy and related to solidification theory. Work to date has been on low melting point alloys and apparatus is under construction to extend the work to high temperature materials. A second part of the study involves levitation melted samples which are undercooled by varying and controlled amounts before being rapidly solidified by splat cooling. This work is being conducted on nickel base alloys.

Sponsor: National Aeronautics and Space Administration

Staff: G. Abbaschian, Y. Shiohara

Graduate Students: G. Chu, R. Ewasko

Theses:

1. M. L. Putman, "Second Phase Measurements in Rapidly Solidified Aluminum-Copper", S.M., February 1981.
2. H. S. Cairnie, "Quantitative Determination of Nonequilibrium θ Phase in Rapidly Solidified Al-Cu", S.M., December 1980.

Publication:

1. H. S. Cairnie, G. J. Abbaschian, M. C. Flemings, "Determination of Nonequilibrium θ phase in Rapidly Solidified Al-Cu", to be published.

4. RAPID SOLIDIFICATION OF THERMOPLASTICS (F. J. McGarry)

The free volume content in glassy thermoplastics depends upon the rate of cooling through the glass transition temperature. It strongly affects certain macroscopic mechanical properties via the process known as aging. Very rapid cooling and solidification of metals has produced amorphous structures with unusual properties. The purpose of the present research is to look for similar effects in glassy polymers containing abnormally large free volume. Some exploratory work with crystalline

polymers may be done also. Careful measurements on quenched thin films of polyvinylchloride and polystyrene do show a significant increase in free volume as compared with control specimens.

Sponsor: National Aeronautics and Space Administration

Faculty: F. J. McGarry

Staff: J. R. Mandell

Graduate Students: H. Lee, V. Agrawal

5. OXIDATION BEHAVIOR OF RAPIDLY SOLIDIFIED ALLOYS
(G. J. Yurek)

The objective of this program is to develop fine-grained rapidly solidified (RS) alloys that are very resistance to isothermal and cyclic oxidation, (sulfidation, carburization, etc.) at elevated temperatures and that contain relatively low concentrations of alloying elements. The program is directed to determining how materials processing (rapid solidification and thermal-mechanical treatments) can be employed to control the microstructures of alloys to enhance their resistance to high-temperature oxidation. An undergraduate student has measured the resistance to oxidation of an RS 18-8 stainless steel. The results demonstrate that RS alloys exhibit superior resistance to oxidation compared with conventional wrought alloys of the same composition. Investigations of the oxidation resistance of rapidly solidified Ni-Al and Fe-Al alloys has been initiated.

Sponsors: Exxon Educational Foundation, M.I.T. Materials Processing Center

Faculty: G. J. Yurek

Staff: A. Garratt-Reed

Graduate Student: D. Cocke

Undergraduate Students: D. Eisen, A. Pendley

Publication:

1. G. J. Yurek, D. Eisen and A. Garratt-Reed, "Oxidation Behavior of a Fine-Grained Rapidly Solidified 18-8 Stainless Steel", to be published.

WELDING RESEARCH

Faculty: T. W. Eagar
D. E. Hardt
K. Masubuchi
H. M. Paynter
J. Szekely
K. Terai (visiting)
W. C. Unkel

SUMMARY

Although continuously present for many decades the welding research effort at MIT has expanded rapidly in the past five years. Presently, this constitutes the largest academic program in welding in the United States. It is led primarily by Professors K. Masubuchi and T. W. Eagar who study Welding Fabrication and Welding Processes, respectively. A number of other faculty are actively involved in many ways, creating an interdisciplinary effort centered in the Departments of Ocean Engineering, Mechanical Engineering and Materials Science and Engineering, and Materials Processing Center.

Personnel include seven faculty, five research scientists and engineers, three technical staff members, eighteen graduate students, and eight undergraduate students. A selection of the ongoing research is presented below.

1. WELDING FABRICATION

The research effort during the period from October 1, 1979 through September 30, 1980 centered around the following four projects:

1. Residual Stresses and Distortion in Structural Weldments in High-Strength Steels.
2. Improved Reliability of Welding by In-Process Sensing and Control (Development of Smart Welding Machines for Girth Welding of Pipes)

3. Development of Joining and Cutting Techniques for Deep-Sea Applications
4. Advanced Welding Technology.

Further details of the research activities are described in the following pages. The Kawasaki Heavy Industries Research Fund also provided financial assistance in conducting research on welding fabrication.

An important accomplishment was the publication of a book entitled Analysis of Welded Structures: Residual Stresses, Distortion, and Their Consequences written by Professor Masubuchi. This book, which has been published by Pergamon Press, covers a wide range of subjects related to the design and fabrication of welded structures. The book has been prepared from a monogram which was originally developed under a research contract entitled "Development of Analytical and Empirical Systems of Design and Fabrication of Welded Structures" sponsored by the Office of Naval Research.

A Ship Structure Committee report (SSC-296) entitled "Review of Fillet Weld Strength Parameters for Shipbuilding" was published in April 1980 covering the results obtained in a research contract sponsored by the U.S. Coast Guard under contract No. DOT-CG-71455-A. The work was completed in May, 1979.

Residual Stresses and Distortion in Structural Weldments in High-Strength Steels

The objective of this research program, which started on December 1, 1977, is to study analytically and experimentally residual stresses and distortion in structural weldments in high-strength steels. The program includes the following two tasks:

- Task 1: Research on thick butt welds.
- Task 2: Research on girth welds of cylindrical shells.

The work performed includes (1) generation of experimental data and (2) development of analytical systems. The primary material investigated was one-inch thick HY-130 steel plates, while some experiments were conducted on low-carbon steel. Experiments in Task 2 were conducted with HY-130 steel plates 3/4 inch thick. Experiments were conducted with the gas metal-arc (multipass) and electron-beam (one or two passes) processes, while some experiments were made using the laser process.

Sponsor: Office of Naval Research

Faculty: K. Masubuchi

Staff: A. Imakita (visiting), A. J. Zona

Graduate Students: J. Agapakis, G. A. Coumis, E. Goncalves, G. A. Mylonas, V. J. Papazoglou, S. K. Platis, P. A. Sa, and A. F. Suchy

Research Report: Technical Progress Report on "Study of Residual Stresses and Distortion in Structural Weldments in High-Strength Steels" by V. J. Papazoglou and K. Masubuchi to ONR under Contract No. N00015-75-0469, November 1979.

Theses:

1. G. A. Coumis, "An Experimental Investigation of the Transient Thermal Strain Variation and the Triaxial Residual Stress Field Generated Due to Electron-Beam Welding of Thick HY-130 Plates".
2. E. Goncalves, "Investigation of Welding Heat Flow and Thermal Strain in Restraint Steel Plates".
3. G. A. Mylonas, "Experimental Investigation of Residual Stress Distributions in Thick Welded Plates".
4. S. K. Platis, "A Study on the Longitudinal Deflection of Fillet Welded Tee Steel Beams".
5. A. F. Suchy, "Investigation of Temperature Distribution and Thermally Induced Transient Strains in Highly Restrained, Thick, HY-130 Steel Plate Weldments".

Publication:

1. K. Masubuchi, "Models of Stresses and Deformation Due to Welding, A Review", Engineering Foundation Conference on Modeling of Casting and Welding Processes, Franklin Pierce College, Rindge, New Hampshire, August 4-8, 1980.

Improvement of Reliability of Welding by In-Process Sensing and Control (Development of Smart Welding Machines for Girth Welding of Pipes)

The overall objective of this three-year research program, which started on June 15, 1979, is to improve the reliability of welding by developing "smart" welding machines. A smart welding machine is equipped with sensors, artificial intelligence and actuators with the goal of reducing welding errors by one or two orders of magnitude. Although the concepts and techniques which will be developed in this program will have more general applications to welding, this research program is focussed specifically on welding of pipes.

Sponsor: Department of Energy

Faculty: D. E. Hardt, K. Masubuchi, H. M. Paynter, and W. C. Unkel

Graduate Students: M. Connaughton, J. Converti, and Y. Dror

Research Reports: First and Second Progress Reports on "Improvement of Reliability of Welding by In-Process Sensing and Control (Development of Smart Welding Machines for Girth Welding of Pipes)" to the Department of Energy under Contract No. DE-AC02-79ER10474.A000), November 1979 and March 1980.

Development of Joining and Cutting Techniques for Deep-Sea Applications

The objectives of this four-year research program, which started on July 1, 1976, are (1) to generate basic information pertinent to joining and cutting techniques for deep-sea applications and (2) to develop some prototype tools suitable for underwater joining and cutting for deep-sea applications. The program from July 1979 through June 1980 covers the following tasks:

- Task 6-2: Development of a Prototype Tool Using Flux-shielded Process
- Task 7: Operational Characterization of Deep-Sea Construction and Repair
- Task 8: Preparation of the Final Report

Sponsor: National Sea Grant Office, National Atmospheric and Oceanic Administration, Department of Commerce

Faculty: K. Masubuchi

Staff: A. J. Zona

Graduate Students: L. Lombardi and D. W. Schloerb

Research Report: A final report is under preparation.

Thesis:

1. J. Lombardi, "Design and Construction of a Portable Welding Machine".

Advance Welding Technology

This research program includes the following subjects:

1. Underwater welding and cutting.
2. Use of computers in the advancement of welding technology.
3. Development of analytical and empirical systems for evaluating the reliability of welded structures.

The research program, which started on April 1, 1977, was originally scheduled for three years. The program has been extended for another year to complete the program.

Sponsors: A group of industrial sponsors including Framatome, Hitachi Shipbuilding and Engineering Co., Ishikawajima-Harima Heavy Industries, Kawasaki Heavy Industries, Kobe Steel Works, Mitsubishi Heavy Industries, Mitsui Engineering and Shipbuilding Co., Nippon Kokan Kaisha, Nippon Steel Corporation, and Sumitomo Heavy Machineries Co.

Faculty: K. Masubuchi and K. Terai (visiting)

Staff: A. Imakita (visiting) and M. Kato (visiting)

Graduate Students: J. Agapakis and V. J. Papazoglou

Research Report: Second Interim Report on "Advanced Welding Technology", March 1980.

Publications:

1. K. Masubuchi, "Applications of Numerical Analysis in Welding", Welding in the World, Vol. 17, no. 11/12, 1979, pp. 268-291.
2. K. Masubuchi, and V. J. Papazoglou, "Current Trends in Welding Technology", presented at the First Cairo University Conference on Mechanical Design and Production, Cairo, Egypt, December 27-29, 1979.
3. M. Kutsuna, K. Masubuchi, H. Nagai, S. Susei, and K. Terai, "Current Problems and Future Prospects in the Application of High-Power Electron-Beam Welding", a paper presented at the International "Beam Technology" Conference, Essen, Federal Republic of Germany, May 7-8, 1980.
4. K. Masubuchi, "Fracture Mechanics Approach to the Characterization of New Welding Procedures", presented at the International Conference on Analytical and Experimental Fracture Mechanics, Rome, Italy, June 23-27, 1980.

2. WELDING PROCESSES

The major thrusts of the new program include:

- Fluxes
- Heat and fluid flow, and
- Sensors for automation.

The majority of the research is concerned with arc welding although studies of resistance spot welding and laser welding are underway. These topics are described in greater detail below.

Flux Development

Flux shielded welding processes account for the largest quantity of welded products; yet our understanding of the flux chemistry and slag-metal reactions remains poor. Reactions involving manganese, silicon, chromium and oxygen are being studied in fused and bonded submerged arc fluxes. A thermodynamic analysis of the slag-metal equilibrium has been developed and tested with remarkable success.

Investigation of active fluxes and flux-cored electrodes is planned. Studies of halide fluxes for use with titanium have shown a number of advantages. Submerged arc welding, gas tungsten arc and electroslog welding of titanium are all being studied.

Sponsors: National Science Foundation, Office of Naval Research, Welding Research Council

Faculty: T. W. Eagar

Staff: A. Block-Bolten, B. Russell

Graduate Students: S. K. Fan, U. Mitra

Undergraduate Students: C. Huntington, P. Kemp

Thesis:

1. C. S. Chai, "Slag Metal Reactions During Flux Shielded Arc Welding", Ph.D., September 1980.

Publications:

1. T. W. Eagar, "Sources of Weld Metal Oxygen Contamination During Submerged Arc Welding", Welding Journal, March 1978, p. 76-s.
2. T. W. Eagar, "Oxygen and Nitrogen Contamination During Arc Welding", in Welding-Physical Metallurgy and Failure Phenomena, R. J. Cristoffel, ed., General Electric Co., Schenectady, New York, 1979, p. 31.
3. C. S. Chai and T. W. Eagar, "The Effect of SAW Parameters on Weld Metal Chemistry", Welding Journal, March 1980, p. 93-2.
4. T. W. Eagar, "Oxygen and Nitrogen Contamination During Submerged Arc Welding of Titanium", to be published in the Proceedings of the International Conference on Welding Research in the 1980's, The Welding Institute, Osaka, Japan, October 1980.
5. C. S. Chai and T. W. Eagar, "Slag-Metal Equilibrium During Submerged Arc Welding", accepted by Met. Trans.

Heat and Fluid Flow

A number of investigators have provided heat flow models for welding involving a moving point source of heat. While this

approximation works well away from the source, it produces erroneous predictions near the weld pool. A comprehensive model allowing for a more realistic distributed heat source is being developed. Both theory and experiment show that the size of the weld pool and the HAZ can vary by a factor of two or more for equivalent heat inputs.

Studies of fluid flow in the welding arc plasma and the molten weld pool are underway. The bulk of this work is theoretical. Some experimental studies of the effects of convection on the size and shape of the weld pool are underway.

A comprehensive model of heat and fluid flow in electrosag welding has been completed and tested experimentally. This study indicates that there is little opportunity to vary the size of the heat affected zone by altering the welding process parameters.

The mechanism of heat transfer during laser welding of aluminum is being studied by measurements of reflectivity and plasma formation as functions of surface preparation and alloy content. Initial results indicate differences of a factor of 20 in the initial heat transfer rate depending on the particular alloy and surface preparation.

Sponsors: Department of Energy, Office of Naval Research

Faculty: T. W. Eagar, J. Szekely

Staff: C. Allemand, A. Block-Bolten, J. McKelliget

Graduate Students: M. Lin, N. S. Tsai

Undergraduate Students: N. Dudziak, C. Huntington

Theses:

1. R. B. Thompson, "Measuring Weld Pool Surface Depression by Photogrammetry", S.B., June 1980.
2. T. D. Burleigh, "Measurement of the Arc Force in GTA Welding", S.M., September 1980.

3. W. S. Ricci, "Heat and Fluid Flow in Electrosag Welding", S.M., September 1979.

Publications:

1. A. H. Dilawari, J. Szekely and T. W. Eagar, "Electromagnetically and Thermally Driven Flow Phenomena in Electrosag Welding", Met. Trans. B, September 1978, p. 371.
2. A. H. Dilawari, T. W. Eagar and J. Szekely, "An Analysis of Heat and Fluid Flow Phenomena in Electrosag Welding", Welding Journal, January 1978, p. 24-s.
3. J. Szekely and T. W. Eagar, "A Mathematical Model of Heat and Fluid Flow Phenomena in Electrosag Welding", Proceedings of Internat. Inst. of Weld. Coll. on Applications of Numerical Techniques in Welding, Dublin, July 1978.
4. C. W. Chang, J. Szekely and T. W. Eagar, "The Analysis of Magnetohydrodynamics and Plasma Dynamics in Metals Processing Operations", Proceedings of the Sagamore Conference on Recent Advances in Metals Processing, July 17-21, 1977.
5. C. W. Chang, J. Szekely, and T. W. Eagar, "The Modelling of Gas Velocity Fields in Welding Arcs", Proceedings of Conference in Arc Physics and Weld Pool Behavior, The Welding Institute, London, May 8-10, 1979.
6. T. Deb Roy, J. Szekely and T. W. Eagar, "Heat Generation Patterns and Temperature Profiles in Electrosag Welding", to be published in Met. Trans.
7. T. Deb Roy, J. Szekely and T. W. Eagar, "Temperature Profiles, the Size of the Heat Affected Zone and Dilution in Electrosag Welding", accepted by Met. Trans.

Sensors for Automation

The greatest difficulty encountered in automating the welding process lies in the selection of useful sensors to monitor the process. In terms of arc welding, monitoring techniques using the thermal and chemical properties of the plasma itself are being developed. Digital processing of the noise signal from a gas tungsten arc has been used to detect defects as small as one-sixteenth inch.

Resistance spot welding is being monitored through the dynamic resistance between the welding electrodes. Other

studies of the effect of surface preparation on resistance spot welding of HSLA steels have led to a patent application for a method of increasing the weldability of these weight saving materials.

Sponsors: Office of Naval Research, National Aeronautics and Space Administration, Bethlehem Steel Corp.

Faculty: T. W. Eagar

Staff: C. Allemand, A. Block-Bolten

Graduate Student: J. G. Kaiser

Undergraduate Students: N. Dudziak, A. Lynch, R. Shoder

Theses:

1. J. G. Kaiser, "The Effect of Electrical Resistance on Nugget Formation During Spot Welding", S.M., February 1981.

Publication:

1. T. W. Eagar, "Automated Welding - Research Needs", to be published in Proceedings Conference on Computer Application in Solidification and in Welding, Rindge, New Hampshire, August 1980.

METALS PROCESSING

Faculty: B. L. Averbach
J. L. Bostock
M. Cohen
M. L. A. MacVicar
R. M. N. Pelloux
R. M. Rose

Staff: S. F. Cogan
G. B. Olson
I. M. Puffer

SUMMARY

The metals processing effort is directed towards improvement of performance and usefulness of materials through modification and control of shape and internal structure. This includes the efforts of Prof. Rose and co-workers to develop reliable, multifilamentary superconducting materials with improved mechanical and electrical properties. Prof. Rose is also working to improve the stoichiometry of recently synthesized Nb_3Si superconductors with an A15 crystal structure. Prof. Cohen and Dr. Olson are concerned with the martensitic transformation-induced plasticity of sheet steels and how this can be applied to improve sheet steel formability. Prof. Averbach is investigating the influence of surface conditions on the basic mechanisms of carburizing high alloy steels. Prof. Pelloux is conducting a systematic investigation of the influence of processing parameters on the crystallographic textures in Zircaloy tubing which determine mechanical and corrosion properties. Prof. MacVicar and co-workers is concerned with replacing precious metals in electrical contact and connector applications with more cost-effective, innovative materials. These research activities are presented in more detail below.

Fabrication of Advanced Multifilamentary Superconducting Composites

The goal of this project is to develop reliable superconducting materials for use in the confinement of fusion plasmas. Mechanical and superconducting properties are both crucial, and processing technologies suitable for the large tonnages to be required are yet to be developed. One substantial processing problem, the development of Kirkendall porosity, was dealt with by either of two methods: solution pre-annealing or by diffusion annealing under modest pressures. Success in this area has removed a major obstacle to the external diffusion technique, which is in turn the key to large scale production of superconducting wire with Nb_3Sn filaments. In addition, the materials thus produced have superior properties.

Microfilamentary superconducting composites of Nb_3Sn fibres in bronze matrices were produced by the external diffusion method together with a solution preanneal to suppress Kirkendall porosity. The resulting materials had superior superconducting and mechanical properties at 4.2°K, carrying overall current densities well over 10^4 amps/cm² at 15.4 T even for low (12%) superconductor fractions; over 10^5 amps/cm² at 12 T; and tolerating (in some cases) strains of the order of 2% without degradation and stresses in the 500-1000 MPa range.

There is evidence that finer superconducting filaments can tolerate much greater intrinsic strains without degradation; also, that the composites investigated were not optimized in terms of residual stresses, matrix composition or filament spacing or size, so that further improvements are possible.

The static and dynamic mechanical behavior of multifilamentary composites is controlled to a significant degree by the

residual stresses, which we have been able to control in turn by thermomechanical processing.

Due to the fact that all of the high-field superconductors are intermetallic compounds, brittleness is a major concern. The specific effects of structural defects and microstructure on the mechanical properties of ZrV_2 (a Laves phase superconductor which is radiation-damage-insensitive) have been investigated from room temperature to 4.2°K.

Sponsor: Department of Energy

Faculty: R. M. Rose, J. L. Bostock, M. L. A. MacVicar

Staff: S. F. Cogan, I. M. Puffer

Graduate Students: A. Hezaveh, J. D. Klein, S. J. Kwon

Undergraduate Students: J. Bowen, N. Dudziak, J. Parse
G. Warshaw, W. Zwirble

Publications:

1. J. Bostock, M. Wong, M. L. A. MacVicar, and M. Levinson, "An Elastic Neutron Diffraction Study of Transforming and Nontransforming Single Crystal ZrV_2 ", Superconductivity in d- and f-band Metals, ed. H. Suhl, M. B. Maple, Academic Press (New York, 1980), pp. 165.
2. S. Cogan, D. S. Holmes, and R. M. Rose, "On the Elimination of Kirkendall Voids in Superconducting Composites", Appl. Phys. Lett., Vol. 35, No. 7, October 1979, pp. 557-559.
3. S. Cogan, D. S. Holmes and R. M. Rose, "Microfilamentary Superconducting Composites by the External Diffusion Method: Nb_3Sn ", J. Appl. Phys., Vol. 51, No. 8, August 1980, pp. 4332-4337.
4. S. F. Cogan and R. M. Rose, "Fatigue Effects in Unidirectional Composites: Applications to Nb_3Sn Superconductors", Appl. Phys. Lett., Vol. 35, No. 11, December 1979, pp. 884-886.
5. S. F. Cogan and R. M. Rose, "Crystallographic Texturing in Nb_3Sn Multifilamentary Superconducting Composites", J. Appl. Phys., February 1980, pp. 1711-1713.
6. S. F. Cogan and R. M. Rose, "Properties of CuSn Bronze at 4.2°K", Cryogenics, June 1980, pp. 313-316.

7. S. F. Cogan, D. S. Holmes, J. D. Klein, and R. M. Rose, "Multifilamentary Nb₃Sn by an Improved External Diffusion Method", Proceedings of ICMC Brookhaven National Laboratories, Mary 1980.
8. J. DeBroux, V. Diadiuk, J. Bostock and M. L. A. MacVicar, "Preferred Orientation and Lattice Registry Effects in Nb₃Sn Diffusion Layers", Superconductivity in d- and f-band Metals, Academic Press (New York, 1980), p. 259.
9. D. E. Moncton, J. D. Axe, J. Bostock and M. Levinson, "Charge Density Waves in the Cubic Laves Phase Superconductor ZrV₂", Bull. Am. Phys. Soc., Vol. 25, 1980, p. 199.
10. K. M. Ralls, R. M. Rose and J. Wulff, "High-Field Superconductivity in the Nb-Ti-Zr Ternary System", J. Appl. Phys., Vol. 51, No. 6, June 1980, pp. 540-544.
11. H. Wada, K. Tachikawa and R. M. Rose, "A Metallurgical Study on Superconducting Ti-Nb Binary and Ternary Alloys", 4th International Conference on Titanium (Japan, 1980).

Synthesis of High Transition Temperature Superconductors by Iron Implantation

The goal of this project is to synthesize the legendary superconductor Nb₃Si in the A15 crystal structure, which is expected to have a very high T_c. The method is to use epitaxial recrystallization of a heavily ion-implanted surface layer.

Following the successful synthesis of "Nb₃Si" with the A15 crystal structure by ion implantation with a conventional machine and annealing in an Al-depleted surface layer, we attempted to improve the stoichiometry by implanting in the Argonne heavy-ion accelerator, which is capable of much higher fluxes. Higher silicon contents were also achieved in the Nb₃(Al,Si) system by improved powder technology.

The effects of carbon addition in the range 1-3% to Nb₃Al was explored, with reference to the kinetics and equilibria for formation of the A15 phase. Additions ca. 1% drastically

reduced the grain size and increased T_c slightly. Additions ca. 2% decreased T_c but accelerated the ordering reaction in the Al5 phase, both effects probably being due to the tendency of carbon to stabilize sigma phases.

Sponsor: Office of Naval Research

Faculty: R. M. Rose

Staff: I. M. Puffer

Graduate Students: J. Adams, E. E. Frey, Jr.

Theses:

1. J. Adams, "Superconductivity in Ion-Implanted Al5 Compounds", S.M., June 1980.
2. E. E. Frey, "Superconductivity in the Nb-Al-C System", S.M., June 1980.

Publication:

1. M. Clapp and R. M. Rose, "On the Synthesis of Metastable A-15 'Nb₃Si' by Ion Implantation and on Its Superconducting Transition Temperature", J. Appl. Phys., Vol. 51, No. 1, January 1980, pp. 540-544.

Transformation-Induced Plasticity in Sheet Steels

The relation of deformation-induced martensitic transformation to plastic flow behavior has been investigated in high-strength TRIP steels, and the principles developed are being applied to the improvement of formability in sheet steels. Current research is directed toward fully austenitic stainless steels as well as low-alloy "Triple-Phase" steels containing small amounts of metastable austenite. Future plans include the development of manganese-stabilized metastable austenitic sheet steels for automotive applications. Stress-state effects and fracture toughness are being investigated in high-strength TRIP steels.

Sponsors: Office of Naval Research, National Science Foundation, Kawasaki Steel Corporation, CNEN (Brazil)

Faculty: M. Cohen

Staff: G. B Olson

Graduate Students: T. Narutani, R. Leal

Publications:

1. G. B. Olson and M. Cohen, "Stress-Assisted Isothermal Martensitic Transformation and Transformation Plasticity", Proc. U.S./Japan Seminar on Mechanical Behavior of Metals and Alloys Associated with Displacive Phase Transformations, RPI (Troy, New York), 1979, p. 7.
2. G. B. Olson, R. Chait, M. Azrin, and R. A. Gagne, "Fatigue Strength of TRIP Steels", Met. Trans. A, Vol. 11A, 1980, p. 1069.

Carburizing of High Alloy Steels

A joint research program with the Fafnir Bearing Company and the General Electric Company is underway on the carburizing of high alloy steels for applications as aircraft gas turbine bearings. The basic mechanisms of carburizing, particularly the surface reactions, are being studied here, in an effort to understand why the carburization of these materials requires special pretreatments to avoid erratic carbon penetration. Surface reactions with various carburizing atmospheres will be studied by means of SAM and ESCA.

Sponsors: Wright Air Development Center

Faculty: B. L. Averbach

Crystallographic Texture Control in Zircaloy Tubes

Mechanical properties, stress-corrosion cracking resistance, and irradiation creep resistance of zircaloy cladding tubes can all be improved by taking advantage of crystallographic texture effects. The fundamental objective of this program

is to conduct a systematic investigation of the manufacturing parameters which control the formation of crystallographic textures in Zircaloy-2 and -4 tubing. Precise control of texture development during tube production must be based on: (1) close observation and detailed analysis of the process, and (2) a thorough understanding of the deformation behavior of the material. In order to accomplish these tasks, samples of Zircaloy from intermediate stages in the tube rocking process are being analyzed dimensionally, microstructurally, and crystallographically. In addition, mechanical tests simulating the deformations incurred during tube production are being performed with similar analyses. The texture sharpening and rotation during the intermediate recrystallization steps is also being evaluated. The main goal of this research program is to achieve process control in the formation of crystallographic textures.

Sponsor: Exxon Nuclear Company, Inc.

Faculty: R. Pelloux

Graduate Student: J. Shewbridge

Precious Metals Elimination Initiative

An investigation is underway to determine the feasibility and desirability of mounting a collaborative MIT/Industry consortium effort to pursue mutually desirable avenues of research with the objective of reducing or eliminating the use of precious metals in standard electrical contact and connector applications. Activities which duplicate lines of inquiry currently being pursued within industrial laboratories or which have been found unproductive in the past would have low priority in comparison to activities relating to more exotic, longer-range, innovative approaches, e.g., intercalated graphite, integrated composites, surface treatments, preferred orientation

processing, etc. The immediate task is to discover the existence of MIT/Industry joint interest in a consortium, and, if positive, to identify member industry candidates and to develop a mutually desirable research agenda and format.

Faculty: J. L. Bostock, M. L. A. MacVicar, R. M. Rose

Graduate Student: Y. Epps

Undergraduate Student: R. Jaimes

MATERIALS SYSTEMS ANALYSIS

Faculty: M. B. Bever
J. P. Clark
A. E. Church
J. F. Elliott
M. C. Flemings
N. J. Grant
J. H. Holloman
T. B. King
D. R. Sadoway
J. Szekely
M. B. Zimmerman

Staff: G. B. Kenney
S. M. Mathur
F. R. Tuler

SUMMARY

Recognizing the need to better understand the societal, economic, and policy tradeoffs associated with materials processing and utilization, the Materials Systems Analysis Group was established within the Department of Materials Science and Engineering in 1975. The principal purpose of the materials systems effort is to provide the materials engineer with the systems analysis required to formulate sound materials processing, utilization, and resource development policies and strategies for private industry and government.

The interdisciplinary research on materials systems analysis involves the collective efforts of 11 faculty members, 5 research staff members, 10 graduate students, and 6 undergraduates from the Departments of Materials Science and Engineering, Sloan School of Management, and Centers for Materials Processing and Policy Alternatives. Prof. Clark continues to expand his innovative materials system simulation and modeling research program which includes assessments of materials substitution dynamics, public policy implications, and materials process economics. This effort includes several collaborative programs with materials engineers, economists, and policy analysts. Prof. Bever coordinates an ongoing program concerned with the technical and socio-economic issues of materials recycling.

The major thrust areas in materials systems research are outlined below.

RESEARCH AREAS

1. MATERIALS SUPPLY AND DEMAND

The foundation of the materials systems analysis program is based on a comprehensive knowledge of materials processes and process technologies. The focus on production economics combines this materials background with quantitative assessments of process developments and policy implications. Specifically, computer simulations have been developed to study the influence of technological changes, economic forces, and public policies on the future raw materials, energy, and capital needs of the U.S. steel industry. Given this assessment of technical alternatives, raw material and energy needs, and related supply/demand sector interactions, subsequent simulation models have been developed to forecast the future supply and demand for products such as stainless steel. Similar studies based on this methodology have been conducted to evaluate the economic viability of expanded magnesium production and utilization and of mining and processing manganese nodules. The framework of this engineering/economic assessment methodology continues to be refined and expanded to other materials systems.

Sponsor: U.S. Bureau of Mines, U.S. Department of Energy,
National Science Foundation

Faculty: M. B. Bever, J. P. Clark, J. F. Elliott, M. C.
Flemings, T. B. King, D. R. Sadoway, J. Szekely

Staff: G. B. Kenney

Graduate Students: J. J. Tribendis, P. T. Foley, D. Richards
P. Baverstam, J. Black, B. Gillenwater,
J. Neuman

Publications

1. F. E. Katrak, T. B. King and J. P. Clark, "Analysis of the Supply of and Demand for Stainless Steel in the United States," *Materials and Society*, Vol. 4, pp. 427-435, 1980.
2. F. E. Katrak and J. P. Clark, "An Analysis of the Determinants of Stainless Steel Pricing and Imports in the United States: Part I - Pricing," *Materials and Society*, Vol. 4, pp. 437-445, 1980.
3. J. P. Clark and F. E. Katrak, "An Analysis of the Determinants of Stainless Steel Pricing and Imports in the United States: Part II - Imports," *Materials and Society*, Vol. 4, pp. 447-455, 1980.
4. J. F. Elliott, J. P. Clark, J. J. Tribendis and C. B. Baldwin, "Computer Modeling of the Impacts of Technological and Policy Alternatives on the Domestic Iron and Steel Industry," Final Report to the U.S. Bureau of Mines under Contract No. J0188010, October 1980.
5. J. P. Clark and F. R. Tuler, "Research and Development Opportunities," in *Materials in World Perspective*, D. Altenpohl, ed., Springer-Verlag, Berlin, 1980.
6. G. B. Kenney and J. P. Clark, "An Analysis of the Potential for Expanded Production and Utilization of Magnesium in the United States," submitted to *Materials and Society*.
7. J. P. Clark, N. J. Grant and T. B. King, "The Potential for Utilization of Manganese from Deepsea Nodules by the U.S. Steel Industry," accepted for publication in *Natural Resources Forum*.
8. F. E. Katrak, T. B. King and J. P. Clark, "An Engineering and Economic Analysis of the Supply of Stainless Steel by the Domestic Industry," accepted by *Materials and Society*.
9. P. T. Foley and J. P. Clark, "U.S. Copper Supply: An Economic/Engineering Analysis of Cost-Supply Relationships," accepted by *Resources Policy*.
10. C. Baldwin, J. J. Tribendis and J. P. Clark, "A Financial Analysis of Investment in the U.S. Steel Industry," accepted by the *Journal of Industrial Economics*.
11. J. R. H. Black and J. P. Clark, "A Financial Analysis of the Profitability of Recovering Metallic Values from Deepsea Nodules," submitted to the *Journal of Policy Modeling*.
12. J. R. H. Black, T. B. King and J. P. Clark, "An Analysis of Four Potential Processing Schemes for Recovering Metallic Values from Deepsea Nodules," submitted to *Materials and Society*.

2. MATERIALS SUBSTITUTION

Quantitative models of intermaterial competition and substitution are being constructed for a number of materials and end use consumption sectors. These simulation models which are based on the dynamic interactions of supply, demand, and price for competing materials are being developed to provide a framework for analysis of relationships between materials supply and demand, the economy, environment, and public policy. Econometric models of the substitution between aluminum and copper in the electrical sector, and magnesium versus aluminum in the automotive sector have been developed. Efforts are continuing to improve and expand the framework of substitution models and evaluation techniques.

Sponsors: U. S. Bureau of Mines, National Science Foundation

Faculty: J. P. Clark, M. B. Bever

Staff: G. B. Kenney, S. M. Mathur, F. R. Tuler

Graduate Students: F. Field, M. Cummings, B. Bosy

Undergraduates: P. Schneider, M. Oliveria

Publications:

1. P. Baverstam and J. P. Clark, "A Quarterly Model of the Demand for Stainless Steel in the United States," submitted to Materials and Society.
2. J. P. Clark and G. B. Kenney, "A Dynamic Systems Model of Competition Between Magnesium and Other Materials in the U.S. Automobile Market," submitted to Materials and Society.
3. J. P. Clark and S. Mathur, "An Econometric Model of Substitution Between Copper and Aluminum in the Electrical Sector of the United States," accepted for publication to the Journal of Land Economics.
4. J. P. Clark, J. J. Tribendis and J. F. Elliott, "An Analysis of the Long Term Supply and Demand Balance in the U.S. Ferrous Scrap Market," accepted by the Journal of Environmental Economics and Management.

3. PUBLIC POLICY

Public policy as enunciated by federal, state, and local regulations shapes corporate policies which determine processing strategies and resource development, or the lack thereof. Consequently, public policy is an important endogenous variable and/or tool to the materials systems analyst. One specific study evaluates the effect of public regulations on the U.S. copper industry by developing a methodology for assessing the costs and benefits of regulations.

Sponsors: National Science Foundation

Faculty: J. P. Clark, M. B. Zimmerman, A. M. Church (University of New Mexico)

Graduate Students: P. Foley

Undergraduates: H. Levine

Publications:

1. A. M. Church, P. T. Foley, M. B. Zimmerman, and J. P. Clark, "The Effects of Taxation on the U.S. Coal and Copper Industries," to be published in Materials and Society, Vol. 4, December 1980.
2. J. P. Clark and P. T. Foley, "An Analysis of the Effects of State and Federal Taxation on Investment in the Domestic Copper Industry," Report to the University of New Mexico under subcontract to the National Science Foundation, January 1980.

4. MATERIALS RECYCLING

Current research on the recycling of materials is part of a continuing program started in the early 1970's. This program has been concerned with technical and socio-economic aspects of recycling, specifically the structure of industrial recycling, a systems analysis exploration of recycling, dissipative uses of metals, resource recover from wastes and the recycling of automotive materials; recently the economic analysis of recycling by the methods of input-output analysis was begun.

In the period under review, experimental research on the recovery of nonferrous metals by means of an eddy current separator was continued. This work was aimed at the recovery of aluminum from various waste streams. The recovery of plastics from shredded beverage containers was also investigated with emphasis on the elimination of small particles of nonferrous metals. The research was carried out by three undergraduate students in the laboratories of Raytheon Company under the supervision of Dr. Ernst F. Schloemann as part of the Undergraduate Research Opportunities Program.

Technical, economic and institutional aspects of the recovery of resources from wastes have been analyzed. The recovery of materials and energy from municipal solid waste was of particular interest.

The recycling of automobiles was considered from several points of view. The interaction of the substitution of materials with recycling was examined with special reference to automotive materials. The impacts of current and forthcoming materials and design changes on the technology and economics of the automobile recycling industry were projected.

Recovery of scrap metals was surveyed with emphasis on developments of the last decade. The strategies for conservation of materials - efficient utilization, substitution and recycling - were reviewed.

The production and consumption of twenty-six basic minerals is being analyzed within the framework of multi-regional input-output models of the United States and world economy at the Institute for Economic Analysis, New York University, under the direction of Professor Wassily Leontief. Past input-output models of the United States economy have not incorporated the flow of secondary materials, but this seems essential for any analysis of the future demand for nonfuel minerals. In work carried out in collaboration with Ms. Sylvia Nasar-O'Brien (Institute for Economic Analysis), the application of

input-output analysis to the recycling of six metals in the United States for three scenarios has been examined. An investigation of the recycling of chromium is being completed.

Sponsors: Rockefeller Foundation, Raytheon Company, U. S. Bureau of Mines, and an anonymous grant.

Faculty: M. B. Bever

Undergraduate students: A. D. Pendley, M. Reiner, B. Masi

Publications:

1. E. Schloemann, M. Reiner and A. Pendley, "High Performance Magnetic Separator for Removal of Partially Magnetic Particles from Shredded Waste," I.E.E.E Transactions on Magnetics, Vol. MAG-15 #6, pp. 1532-1534 (1979).
2. E. Schloemann and M. Reiner, "Nonferrous Metal Separators for Small Particles," I.E.E.E Transactions on Magnetics, Vol. MAG-15 #6, pp. 1535-1537 (1979).
3. C. M. Miller and M. B. Bever, "Assessing the Environmental Impacts of Resource Recovery Facilities," Environmental Impact Assessment Review, Vol. 1, pp. 37-52 (1980).
4. M. B. Bever, "Introduction to Materials Recycling" in Materials in World Perspective by D. G. Altenpohl, Springer-Verlag, Berlin 1980, pp. 165 ff.
5. M. B. Bever, "Impacts of Materials and Design Changes on the Recycling of Automobiles," Materials and Society, Vol. 4, pp. 375-385 (1980).
6. M. B. Bever, "Review of Scrap Metal Recovery," Proceedings of the 7th Mineral Waste Utilization Symposium, pp. 173-183 (October 1980).
7. M. B. Bever, "Issues in Materials Economics and Materials Policy," Summary of Lecture given October 4, 1979, Berliner Wissenschaftliche Gesellschaft, 1979 Jahrbuch, pp. 135-138.
8. M. B. Bever, "Conservation Strategies for Materials," Senior Executive Symposium, Industrial Liaison Program, M.I.T., June 26, 1980, Proceedings, pp. 345-355 (1980).
9. Sylvia Nasar-O'Brien and M. B. Bever, "Applications of Input-Output Analysis to Investigations of Metals Recycling," Proceedings, Council of Economics, AIME, 1981 (in press).

TECHNOLOGY TRANSFER AND INTERNATIONAL DEVELOPMENT: MATERIALS
AND MANUFACTURING TECHNOLOGY

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SUMMARY

The Center for Policy Alternatives (CPA) under the directorship of J. Herbert Hollomon has conducted, over the past seven years, a series of policy-oriented studies on technological development in several relatively advanced developing countries. These have been directed by K. Nagaraja Rao. Priority sectors defined in terms of technological sophistication, capital intensity, value added and export potential have been studied in the cases of Brazil, Venezuela, Israel and Korea. A study of the institutional infra-structure and industrial potentials of Portugal, slated to join the Common Market in the mid-1980's, has just been started. These projects have been supported directly by the countries themselves or through loans and grants made to them by international agencies such as the World Bank and the U.S. Agency for International Development. Research teams include graduate students from M.I.T. Schools of Engineering and Management, and senior researchers from the countries sponsoring the study.

Although the objectives of these studies are generally to develop technological policy alternatives for the sponsoring country, much emphasis is placed on understanding the dynamics of the sectors through structure interviews with a large sample of firms in the leading manufacturing and materials processing sectors. Examples of such sectoral studies from current projects are provided below.

Korea Technological Development Project

This project conducted by CPA in collaboration with the Korean Institute of Science and Technology (KIST) undertook a critical examination of the recent technology development policies of the government and an assessment of the public infrastructure in research and development, engineering and standardization. Shipbuilding, automotive, electric power generation equipment and chemical process industry sectors were reviewed with a view to assess their present technological level, dependence on imported technology and materials and the needed changes in manufacturing technology for industry to be internationally competitive. Recommendations for technical upgrading of industry are now being implemented through the creation of the Korean Technology Development Corporation.

Sponsors: Industrial Projects Division of the World Bank, The United Nations Industrial Development Program, The Ministry of Science and Technology, Republic of Korea

Faculty: R. Baddour, K. Masubuschi, J. Hollomon, M. Utterback

Staff: K. Rao, T. Hill

Graduate Students: A. Tschoegl, K. Saeed, T. Schmitt

Research Collaborators from KIST: C.-O. Lee, H. C. Kim, S. Z. Oh, B. G. Yoo, C. S. Lee

Publications:

1. K. Masubuchi and H. C. Kim, "Technological Development in the Shipbuilding Industry in Korea", July 1980.
2. H. Mathews, D. Hurter and S.-Z. Oh, "A Technical Assessment of the Korean Automotive Industry", August 1980.
3. E. G. Schwarm, C. S. Lee, C. W. Lee, and J. H. Park, "Technical Assessment of the Korean Electric Power Generation Equipment Industry", June 1980.
4. R. Baddour, "Technological Development in the Chemical Process Industry in Korea", May 1980.

[Other related reports connected with this project include studies of: "Organizational Model for the Support of Industrial Innovation, Entrepreneurial Perceptions on Industrial Innovation in Korea, and a study of Public Industrial Research and Development Institutes in Korea."]

Disarmament and Development: The Case of Relatively Advanced Developing Countries (Possible Economic Payoff from Military Production: The Case of the Aircraft Industries in Brazil, Israel and India)

As part of a study intended to estimate the economic payoff from military production, three in-depth case studies of aircraft production in three relatively advanced developing countries were undertaken. In these studies methods were developed to estimate resources of manpower and materials used in military and civilian aircraft production in these countries and the extent of dependence on imported materials and technology. Impediments to the transfer of production technology were identified as well as policies adopted by the governments to ingest imported technology and to develop local capabilities in design and fabrication.

Sponsor: United National Disarmament Project Fund

Faculty: J. P. Ruina

Staff: K. N. Rao, A. Yarom

Graduate Students: K. Nochur, R. Desourdis

Research Interns: B. Deckenback

Publication:

1. K. N. Rao, J. P. Ruina, R. Desourdis, B. Deckenback, A. Yarom, and K. Nochur, "Disarmament and Development: The Case of Relatively Advanced Developing Countries", CPA-80-05, August 1980.

Remanufacturing in Selected Developing Countries

In industrialized countries, independent firms and specific divisions of equipment manufacturers exist by giving new lives to older durable products. This process is termed remanufacturing and has three basic stages. Initially, a relatively large number of older products are disassembled to make a pool of interchangeable parts. In the second stage, the parts are cleaned and refinished; defective parts are also replaced or re-machined. In the last stage parts are re-assembled on an assembly line to produce products which have performance and life expectancy equal or approximate to brand new goods. Remanufacturing is a big industry in the United States. With the increasing costs of energy and raw materials, remanufacturing has been shown to have even greater potential for contributing to the U.S. economy than before. Research at the Center for Policy Alternatives has centered on the examination of the economic and social benefits of remanufacturing in the U.S. Some preliminary work has been started to investigate the potentials of remanufacturing in selected developing countries.

Sponsors: Proposals being circulated

Staff: R. T. Lund, K. N. Rao

Graduate Students: R. Upaa, A. Deolalikar

Publication:

1. R. Upaa, R. T. Lund and K. N. Rao, "Is Remanufacturing Adaptable to Nigeria", CPA/wp-80-01, January 1980.